Design and systems-level performance analysis of petroleum coke conversion strategies

DESIGN AND SYSTEMS-LEVEL PERFORMANCE ANALYSIS OF PETROLEUM COKE CONVERSION STRATEGIES

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Abstract

Petroleum coke (petcoke) is a solid waste product of crude oil refinery operations with disposal issues. Therefore, this thesis focuses on systems level performance analysis of design configurations by which petcoke can be disposed of in the most environmentally benign and cost-competitive pathway. In the systems evaluated, we explored the environmental and cost benefits of utilizing the energy stored in the refinery solid waste (petcoke) to produce liquid transportation fuels and electricity. Specifically, we proposed petcoke as a feed to produce liquid fuels via Fischer-Tropsch synthesis. For power generation, we explored the performance of petcoke in an integrated gasification combined cycle (IGCC) and oxy-combustion technology. To minimize greenhouse gas (GHG) emissions, carbon capture and sequestration (CCS) were implemented in some of the designs allowing further performance analysis of the variants of the designs which were operated with and without CCS.

In the petcoke to liquid fuels study, three design strategies that operated with and without CCS namely petroleum coke standalone gasification (PSG), petroleum coke gasification integrated natural gas reforming (PG-INGR), and petroleum coke gasification external natural gas reforming (PG-ENGR) were proposed. To compare the performance of the designs, performance metrics such as fuel and thermal efficiencies, net present value, minimum diesel selling price, and direct CO_2 emissions were employed. Overall, the PG-INGR design outperformed the other designs and showed to be a feasible candidate design for petcoke to liquids process.

Subsequently, a cradle-to-grave environmental life cycle impact assessment of a petcoke derived diesel for a functional unit of 1 km distance driven in a diesel-powered vehicle was investigated for two possible locations in Canada: Ontario and Alberta provinces. These petcoke processes were compared to the conventional crude oil and oil sands derived diesel processes. In terms of GHG emissions, the results showed that there was no clear superior design amongst the three CCS enabled processes for the plants located in Ontario, but they outperformed the conventional crude oil and oil sands derived diesel processes.

When the cost of CO_2 avoided (CCA) was factored into the analysis for the petcoke processes, the PG-INGR design had lower costs and thus confirms it as the viable design to adapt for liquids production.

Exploring the benefits of a waste source of fuel, the techno-economic and life cycle analysis (LCA) of petcoke was further examined in the IGCC power plant operated with CCS. This design performance was compared against the coal-based IGCC and supercritical pulverized coal (SCPC) power plants operated with CCS of the same net power output based on its levelized cost of electricity, thermal efficiency, feed consumption rate, and direct GHG emissions. Results showed that the petcoke power plant outperformed both reference systems in both economics and environmental impacts.

Finally, petcoke was further explored as fuel in the oxy-combustion power plant designed to operate with and without carbon capture and sequestration. Our study of the oxy-combustion power plant further included the purification of the captured CO_2 stream via cryogenic distillation to meet pipeline specifications. This analysis was to compare its performance to that of petcoke IGCC power plant. LCA and CCA of the petcoke oxy-combustion power plant designs were also presented. Overall, the results showed a cost-competitive source of electricity generation even for the design with highly purified CO_2. In terms of environmental impacts, the LCA study confirmed the minimal emission tendency of the petcoke oxy-combustion system even when the indirect petcoke emissions were considered.

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This thesis is dedicated to my wife, Chiamaka Rita Okeke, my son, Chikelum Francis Okeke, my mum, Ann Uche Okeke, my siblings, and in the loving memory of my father, Chief Simon N. C Okeke who passed away during the time I was writing this thesis.

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Declaration of Authorship

I, Ikenna Joseph OKEKE, state that I was the main researcher in this thesis titled, "Design and systems-level performance analysis of petroleum coke conversion strategies" and the work presented therein are solely my research contributions. I confirm that:

- the published scholarly work presented as a reprint in Chapter 2 has my full contribution to project conceptualization, investigation and analysis, model development and simulation, and manuscript preparation. In this work, three design strategies operated with and without carbon capture and sequestration were proposed for the conversion of petroleum coke and/or natural gas to liquid fuels, with a competitive minimum diesel selling price when compared to the status quo.

- the published scholarly work presented as a reprint in Chapter 3 has my full contribution to project conceptualization, investigation and analysis, and manuscript preparation. In this work, a novel cradle-to-grave LCA of petroleum coke and natural gas to Fischer-Tropsch diesel process based on the three design configurations operated with and without CCS presented in Chapter 1 was conducted for two locations in Canada: Ontario and Alberta provinces. The reference processes for comparison are the conventional crude oil and oil sands derived diesel. The outcome from this work showed the impact of grid electricity to the overall environmental performance of each design for which the proposed system at low electricity emission outperformed the two reference cases.

- the published scholarly work presented as a reprint in Chapter 4 has my full contribution to project conceptualization, investigation and analysis, flowsheet development and simulation, and manuscript preparation. In this work, the design and LCA of a petroleum coke IGCC power plant operated with CCS was proposed. Comparing the performance of the proposed petroleum coke IGCC power plant to that of the traditional coal-fired power plant, the LCOE for the petroleum coke system was 12% lower, with a cradle-to-gate environmental impact which completely outperformed the coal plant.

- the work presented in Chapter 5, which is a manuscript draft, has my full contribution to project conceptualization, investigation and analysis, flowsheet development and simulation, and manuscript preparation. Petcoke oxy-combustion power plant operated with and without CCS was studied exploring the design and cost feasibility. In addition, a design that examined the trade-offs in costs, efficiency loss, and emissions to achieve a CO_2 pipeline specification via CO_2 cryogenic purification of the captured CO_2 stream was presented. This represents a novel study that completely explored the overall system's performance of a solid fuel oxy-combustion power plant.

- the work presented in Chapter 6, which is a manuscript draft, has my full contribution to project conceptualization, investigation and analysis, flowsheet development and simulation, and manuscript preparation. This is the Part II of the petcoke oxy-combustion power plant operated with and without CCS which examined the cradle-to-customer environmental impact assessment and cost of CO_2 avoided of the designs presented in Chapter 5. The life cycle impact assessments were presented at both the midpoint and endpoint levels which allows for a comprehensive analysis. Altogether, this is a novel analysis that examined the life cycle of petcoke oxy-combustion power plant.

Chapter 1

Introduction

1.1 Background

Traditional crude oil refinery operation produces high-value petroleum products such as gasoline, diesel, fuel oil, etc in addition to bottom of the barrel residual products. To maximize profit, coupled with falling demand for residual oil, refiners further processes the residual products to produce lighter fractions through coking processes; thus producing solid carbon waste known as petroleum coke (also generally known as petcoke). Typical coking processes employed are fluid and delayed coking which differ in the type of thermal processing employed producing different types of petcoke such as needle coke, sponge coke, and honeycomb coke depending on type of crude oil processed, cooking temperature, time of coking, and coking mechanism.

Delayed coking involves the use of two or more coke drums, a heater, and a fractionator for which the fractionator is charged with fresh residual feed through the bottom and subsequently charged with some recycle which passes through the heater and coke drum before entering the fractionator (McKetta Jr 1992; Coker 2018). The temperature of operation is between 432°C and 482°C. The residual flows into the bottom of one of the coke drums where cracking takes place filling the drum with solid coke while the lighter fractions enter the fractionator and leaves as vapor (Coker 2018). The solid coke (petcoke) is collected as a waste product of the coking process. In fluid coking, the residue is fed to a heated continuous reactor where the cracking operation occurs at temperatures between 482°C and 566°C (generally above the temperature of the delayed coke) and at a residence time as short as 15 to 20*s*, producing the lighter fractions and coke (McKetta Jr 1992). The heat of the fluid coking process is provided by burning some of the produced coke while the remaining coke is collected for other downstream purposes.

Depending on the petroleum feedstock used, there are differences in the carbon, volatile matter, and ash contents of different types of petcoke. Table 1.1 shows the ultimate and proximate analysis as well as the energy values of delayed and fluid coke as reported by (Watkinson et al. 1989). As can be seen, petcoke is predominately carbon and thus can produce up to 10% higher CO_2 emission (on an energy basis) than coal when combusted (Stockman 2013). In addition, the sulfur content of petcoke makes it a high emitter of SO_x and when combusted with air, high amount of NO_x are also produced. These are emissions when emitted into the atmosphere can turn into compounds that can form tiny particles and possibly remain in air to considerable amount of time (EPA 2002). Effects of such emission can range from decreased visibility, respiratory illness, water acidification, and as much as loss of live (EPA 2002).

TABLE 1.1: Ultimate, proximate, and heating values of different type of petcoke (Watkinson et al. 1989)

Properties	Delayed coke	Fluid coke
HHV(MJ/kg)	34.7	29.7
Ultimate analysis (wt.%dry)		
C	84.9	79.5
H	3.9	1.6
N	1.3	1.7
S	6.0	7.0
Cl	0	0.7
Ash	0.8	1.2
O (diff)	0.8	1.2
Proximate analysis (wt. %)		
Moisture	1.8	3.7
Volatile matter	11.9	6.9
Fixed carbon	83.3	81.4
Ash	3.0	8.0

In addition to the high carbon and sulfur content of petcoke, ash is another issue associated with petcoke handling and conversion. Table 1.2 presents the composition of ash for the delayed and fluid coke based as reported by (Furimsky 1985). This details the metal oxides composition of the different types of petcoke which could pose environmental challenges when released to the environment. Nevertheless, the energy value of petcoke makes it attractive to use as a solid fuel when compared to coal and biomass. Now, the challenge lies on how effectively petcoke can be converted without adversely affecting the environment.

TABLE 1.2: Ash composition of delayed and fluid coke (Furimsky 1985)

Components	Delayed coke	Fluid coke
SiO_2	42.18	40.78
Al_2O_3	22.72	24.10
Fe_2O_3	11.85	9.11
NiO	1.21	1.16
V_2O_5	4.40	4.28
TiO_2	3.28	2.82
P_2O_5	0.29	0.32
CaO	3.45	5.01
MgO	1.59	1.96
SO_3	2.53	3.93
Na_2O	0.75	1.70
K_2O	1.93	1.87
BaO	0.03	0.14
SrO	0.02	0.07

1.2 Motivation

Typically, petcoke with its high sulfur content is termed fuel grade coke and is sold at a discount to coal for fuel purposes in cement kilns, boilers, etc. However, firing petcoke for energy purposes has been restricted at least in parts of North America (Andrews and Lattanzio 2013) due to the inherent emissions. Hence to dispose petcoke, calcination operation is employed to produce anode-grade petcoke, which is a raw material in the aluminum and steel industries while the remaining produced petcoke (generally unprocessed petcoke) is stockpiled indefinitely which poses a number of problems. Figure 1.1 shows a petcoke stockpile at the Canadian-Detriot border as reported in the New York Times (Austen 2013) which has raised concern amongst residents.

The New York Times

ENERGY & ENVIRONMENT

A Black Mound of Canadian Oil Waste Is Rising Over Detroit

By IAN AUSTEN MAY 17, 2013

RECENT COMMENTS

Maureen66 May 19, 2013
Or as Kate McMillan at www.smalldeadanimals.com notes - let me fix that headline for you.Canadian oil sands provides opportunity to pave...

ThatGuy May 19, 2013
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Juliana Sadock Savino May 19, 2013
Tax it.

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Petroleum coke, a waste byproduct of refining oil sands oil, is piling up along the Detroit River.
Fabrizio Costantini for The New York Times

FIGURE 1.1: Petroleum coke stockpile at Canada-US border (Austen 2013)

Challenges associated with the stockpiling of petcoke includes but not limited to valuable land occupation, and potential adverse effects on human health via air and water pollution, and respiratory health of nearby populations (Andrews and Lattanzio 2013). Petcoke is also a source of fine particulate dust emission that has the tendency of penetrating human respiratory systems which could affect the lungs and result in adverse health challenges (EPA 2013). Its toxicity level has been reported by the EPA to be of low level with no reported evidence of being a cause of carcinogenicity (EPA 2013). Nevertheless, based on its chemical composition, it contains a toxic metal, notably vanadium, which can be found in the dust at petcoke stockpile locations. Clinical health trials using animals with repeated chronic inhalation dosage showed some traits of respiratory inflammation attributed to particulates (Andrews and Lattanzio 2013). Due to the presence of ash in petcoke and given the effects of ash dust such as the potential for lung disease, asthma attacks, and even cancer, these concerns highlight the need for the development of a benign petcoke “end of life” strategy.

Commercial use of petcoke or a combination of petcoke and coal for power generation is by Wabash River Energy Ltd.’s and the Tampa Electric Polk Power Station (Andrews and Lattanzio 2013; DOE 2004). It is worthy to mention that both power plants employ a coal gasifier to convert petcoke to syngas (without operational issues) which drives the gas turbine for electricity generation. One of the advantages of petcoke as a waste solid fuel with zero purchase price is being employed by Coffeyville syngas plant which utilizes petcoke waste from the Coffeyville refinery to produce ammonia (Brown 2013). Over the years, several studies have examined the feasibility of petcoke as a feedstock in a polygeneration system to produce either or a combination of Fischer-Tropsch (FT) liquid fuels, methanol, fuel gas, olefins, hydrogen, dimethyl ether (DME), and industrial-grade steam (Kramer 2003; Salkuyeh and Adams II 2015; Holt and Alpert 2003; Phillips 2007; Lazzaroni et al. 2017). One of the key findings is the inherent advantage of petcoke price as a zero-cost fuel which showed to be competitive. Khojasteh et al., further carried out an optimization study of a petcoke-natural gas polygeneration which the results showed that petcoke-natural gas polygeneration is economical at a certain petcoke/natural gas ratio (80% gas), with the gas-only configuration strongly preferred with the market prices at the time of the study (Salkuyeh and Adams II 2015). A mixed-inter linear programming on a petcoke fueled power-to-gas technology was studied to ascertain the economic feasibility of employing electrolysis and surplus grid electricity for fuels and chemicals (Ranisau et al. 2017) as means of petcoke disposal.

Nevertheless, despite the studies and commercial application of petcoke utilization for power, fuels, and chemicals production, the environmental impacts of such petcoke disposal approach have not been studied. Thus, it has become imperative that the gap in the literature on the life cycle environmental impacts of petcoke conversion is examined.

1.3 Contributions

Thus, the main contribution of this thesis is to develop new petcoke conversion design strategies for process improvement and subsequently evaluate the life cycle environmental impacts of the proposed conversion pathways in order to draw conclusions on the best disposal approach to adapt. Chapter 2 primarily focuses on proposing novel petcoke gasification by integrating natural gas reforming within the petcoke gasification steps in order to analyse the synergy of such integration for possible performance improvements as it compares to the traditional systems. Chapter 3 evaluates the environmental impacts assessment of diesel fuel production and usage based on the designs presented in Chapter 2. Chapter 4 presents a novel analysis of the environmental LCA of the petcoke IGCC power plant which is compared to the coal-fired power plant and coal IGCC power plants. Interests in oxy-combustion due to the ease of CO_2 and H_2O separation necessitates the evaluation of petcoke use as fuel for power generation in an oxy-combustion power plant which the design and economics is presented in Chapter 5 while the life cycle environmental impacts assessment is discussed in Chapter 6. In the final chapter, conclusions and suggestions for future work are outlined.

1.3.1 Strategies for petroleum coke conversion to liquid fuels.

Traditional petcoke conversion generally employs an entrained flow gasifier to convert petcoke or a blend of petcoke/coal to syngas which is a precursor for downstream production of chemical, fuels, etc. Novel petcoke gasification that integrates natural gas reforming within the petcoke gasification steps is presented with the purposing of evaluating the synergy of integrating the hot gasifier heat with the endothermic natural gas reforming as it compares to the traditional systems. In this petcoke to liquids conversion strategy, natural gas is passed through the radiant syngas cooler tightly filled with catalyst to provide the cooling duty and in turn reform the natural gas to syngas; altogether, producing more syngas (petcoke gasifier syngas and natural gas syngas). Employing this design, the steam to carbon ratio is adjusted to achieve the desired H_2/CO such that water-gas shift unit may no longer be required. In addition, the efficiency of syngas production is maximized given the synergy of the integration between the gasifer and the natural gas reformer. The model development of the petcoke gasifier integrated with natural gas reformer was carried out in gProms commercial software which consists of five submodels namely the shell side, tube side, catalyst, tube wall, and refractory models. In order to properly examine the performance of the proposed petcoke gasification integrated with natural gas reforming, two other designs were evaluated namely: the traditional petcoke gasification and petcoke gasification with external natural gas reformer. The latter is chosen to ensure that the bias with regards to having additional feedstock is eliminated. Altogther, the three design configurations were operated at the same thermal energy input for ease of comparison. All the simulations runs were carried out in Aspen V10 simulation environment. The results from this research contribution were published in the peer-reviewed journal Energy, and is presented in Chapter 2 of this thesis.

The full citation of the paper is – Okeke, Ikenna J., and Thomas A. Adams II. "Combining petroleum coke and natural gas for efficient liquid fuels production." Energy 163 (2018): 426-442.

1.3.2 Analysis of the environmental impacts of petroleum coke to liquids processes.

The proposed three design strategies for liquid fuels production operated with and without CCS that was presented in Chapter 2 was used to conduct an environmental impact assessment of petcoke derived diesel. The study presents a novel analysis that evaluated the environmental benefits of using the refinery waste to produce diesel transportation fuel; thus, reducing the use of fossil derived diesel. In this analysis, a comprehensive LCA of the combined petroleum coke and natural gas to diesel process was studied using the updated impact factors of the 5^{th} Assessment Report of the Intergovernmental Panel on Climate Change (IPCC) to commute the impact categories. Ten environmental impacts categories were investigated for multiple locations in Ontario and Alberta, Canada, which represents areas of low and high electricity grid emissions respectively. The life cycle impact assessment was calculated in SimaPro simulation tool using TRACI v2.1 midpoint method. Cost of CO_2 (CCA) avoided was also calculated for the CCS enabled designs to ascertain the extra costs paid for environmental purpose. The proposed petcoke and/or natural gas to diesel process showed to have reduced environmental impacts compared to the conventional crude oil and oil sands processes. In addition, the CCA estimated is lower than the ethanol based system. The results from this research contribution were published in the peer-reviewed journal, International Journal of Greenhouse Gas Control, and is presented in Chapter 3 of this thesis.

The full citation of the paper is – Okeke, Ikenna J., and Thomas A. Adams II. "Comprehensive environmental impact assessment of a combined petroleum coke and natural gas to Fischer-Tropsch diesel process." International Journal of Greenhouse Gas Control 96 (2020): 103012.

1.3.3 Application of petroleum coke disposal to electricity generation: cost and environmental impact assessment of petroleum coke IGCC power plant.

Petroleum coke IGCC power plant was designed with CCS to ascertain the systems performance in terms of feed consumption, thermal efficiency, heat rate, process emissions, and LCOE. This formed the basis for the novel environmental impact assessment of the petcoke IGCC power plant. Compared to the traditional coal-fired power plant, the petcoke IGCC showed that it is a viable feedstock to the IGCC power plant compared to coal. The results from this research contribution were published as conference proceedings in Computer Aided Chemical Engineering after peer-review, and is presented in Chapter 4 of this thesis.

The full citation of the paper is – Okeke, Ikenna J., and Thomas A. Adams II. "Systems Design of A Petroleum Coke IGCC Power Plant: Technical, Economic, And Life Cycle Perspectives." Computer Aided Chemical Engineering. Vol. 47. Elsevier, 2019. 163-168.

1.3.4 Application of petroleum coke disposal to electricity generation: design, economics, and environmental analysis of petcoke oxy-combustion.

Petroleum coke oxy-combustion power plant is proposed as a another avenue for petroleum coke disposal. Designs operated with and without CCS were presented. Furthermore, unlike the coal oxy-combustion studies, a design that analyzes the additional costs and efficiency loss of purifying the captured CO_2 stream to meet pipeline specification was also presented hightlighting the novelty of this work. The simulation of the petcoke oxy-combustion power plant were modeled in Aspen Plus v10. The results of the converged simulation were used to estimate the system's feed consumption rate, thermal efficiency, net power output, and cradle-to-gate GHG emissions. The discounted cash flow rate of return model was carried out using the total capital investment and operating costs to estimate the LCOE of each design at a net present value of zero. The results from this research contribution is presented in Chapter 5 of this thesis. A draft manuscript of the full paper containing contributions from this work has been submitted to the Canadian Journal of Chemical Engineering with the title – Okeke, Ikenna J., and Thomas A. Adams II. "Advanced petroleum coke oxy-combustion power generation with carbon capture and sequestration: Part 1 - Design and Techno-Economic Analysis."

Based on the mass and energy balance of the petcoke oxy-combustion designs presented in Chapter 5, the first-of-its-kind environmental impacts assessment of the "end of life" of petcoke via oxy-combustion power generation operated with and without CCS is presented. The LCIA were calculated using both the TRACI v2.1 and ReCiPe 2016 methods to provide a comprehensive analysis. In addition, using an SCPC plant without CCS as the reference, the cost of CO_2 was calculated to ascertain the parasitic cost of building an oxy-combustion plant operated with CCS. The results of this analysis were compared to our prior work on petcoke IGCC and to the coal IGCC and SCPC studies operated with CCS. In addition, the performance of the petcoke oxy-combustion power plants with CCS was compared to other fossil-fuel power plant technologies operated with CCS. The results from this research contribution is presented in Chapter 6 of this thesis. A draft manuscript of the full paper containing contributions from this work has been submitted to the Canadian Journal of Chemical Engineering with the title – Okeke, Ikenna J., and Thomas A. Adams II. "Advanced Petroleum Coke Oxy-Combustion Power Generation with Carbon Capture and Sequestration: Part II - Environmental Assessment and Cost of CO_2 Avoided."

1.4 Challenges

During this course of this thesis, there were inherent challenges faced in the modeling, simulation, and analysis of this work. Modeling of the petcoke gasification integrated natural gas reformer system was carried out in the algebraic modeling environment provided by gProms. In this modeling environment, the first-principles model of the system in question was described using appropriate thermodynamic and transport property models. Since these models are based on empirical data, they are feasible only for a certain range of operating conditions. Therefore, using such models for extrapolating the system behavior beyond these bounds would lead to incorrect conclusions. Thus, as the petcoke gasification system was operated at about 1426°C, large amounts of experimental data at this operating condition were required to fit an empirical model, which was difficult to find. Furthermore, running each simulation of the system where gProms has to solve a system of discretized partial differential equations can take a long time and is interspersed with convergence issues.

Another challenge encountered in this thesis is process synthesis in Aspen Plus which is used to estimate the mass and energy balance used in cost estimation and life cycle analysis. As the flowsheet developed contains unit operations such as distillation columns and absorbers, convergence is a major issue. In addition, the presence of recycle streams made it even harder to achieve convergence because of the way Aspen Plus handles recycle streams. The choice of a tear stream in Aspen Plus is sometimes arbitrary and has failed in most cases. This was hugely experienced in the modeling of the CO_2 capture in Aspen Plus which has quite a lot of recycles for solvent regeneration. Hence, ProMax was used in this work for the solvent-based CO_2 capture as it has better initial guess and a consistent routine in handling tear streams with ease.

Finally, the lack of quality data on the environmental effects of petcoke stockpile possessed an issue in the overall analysis of this work. Due to the presence of metals in petcoke in addition to its dust, there exists a need to accurately quantify the extent of emissions emanating from petcoke. Data such as dust emissions per kg of petcoke, water damage per kg of petcoke, extent of leaching per kg of petcoke, etc. are lacking which is necessary for the analysis of the petcoke conversion analysis.

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Chapter 2

Strategies for petroleum coke conversion to liquid fuels.

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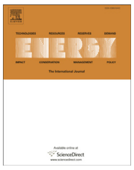

Combining petroleum coke and natural gas for efficient liquid fuels production

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ABSTRACT

This work explores the technical feasibility and economic profitability of converting petroleum coke (petcoke) and natural gas to liquid fuels via Fischer-Tropsch synthesis. Different petcoke conversion strategies were examined to determine the conversion pathway which can be competitive with current market prices with little or no adverse environmental impacts. Three main design approaches were considered: petcoke gasification only, combined petcoke gasification and natural gas reforming through traditional processing steps, and combined petcoke gasification and natural gas reforming by directly integrating the gasifier's radiant cooler with the gas reformer. The designs investigated included scenarios with and without carbon capture and sequestration, and with and without CO_2 emission tax penalties. The performance metrics considered included net present value, life cycle greenhouse gas emissions, and the cost of CO_2 avoided. The design configuration that integrated natural gas reforming with the gasification step directly showed to be the more promising design for the wide range of analyses performed. The Aspen Plus simulation files have been made freely available to the public.

1. Introduction

Despite the current trend towards a shift to green and sustainable energy sources with reduced greenhouse gas (GHG) emissions, the use of fossil energy continues to dominate the world's energy mix. According to the 2017 BP statistical review of world energy, a total primary energy of 13.3 billion tonnes of oil equivalent was consumed in 2016 [1] of which fossil energy contributed 86% of the total.

Over 90% of Canada's oil deposit is made up of heavy oil [2] which leaves between 15% and 40% of the oil as residues in the refinery distillation unit [3,4]. To maximize profit and also meet demands for transportation fuels, refiners further crack these residues in coker units producing unwanted solid carbon material by-product known as petroleum coke (petcoke) [5]. The type of petcoke produced depends on the coker unit used [5]. Fluid and delayed coke are produced in Canada by Syncrude and Suncor respectively [6] with delayed coke getting more industrial attention [7]. Generally, petcoke is classified as either fuel grade or graphite depending on their sulfur content [8] and could be used for wide range of applications such as anode, fuels in kilns, etc. Reports on petcoke availability have ranged between 56 and 150 million tonnes per year (Mt/yr) [4,8]. Recently, stockpiled petcoke produced in Canada by Syncrude, Suncor, and CNRL near Fort McMurray, Alberta is estimated to be about 100 (Mt/yr) [9] with reasons being due to lack of transportation and carbon sequestration [4]. Such a large amount of solid fuel is sufficient to create dedicated power and chemical production facilities solely running on petcoke.

Therefore, just like coal, petcoke can be used for power generation in supercritical pulverized coal (SCPC) or integrated gasification combined cycle (IGCC) plants since it has a competitive heating value of 34.7 MJ/kg [10] and can be obtained at very low cost since it is a waste product. On the downside, petcoke is a dirty fuel with 5–10% higher CO_2 emissions per unit energy produced [4]. Hence, replacing petcoke with coal is obviously not environmentally advisable. However, the conversion of petcoke to make liquid transportation fuels could potentially reduce greenhouse gas emissions by offsetting some petroleum usage. Thus, this study explores petcoke conversion strategies that could be both economically competitive and environmental friendly.

Some studies have examined different commercial plants which use petcoke either alone or in combination with coal for power and chemical productions [11,12]. However, research on the techno-

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economic analysis of petcoke conversion to power, chemicals, and fuels are limited. Orhan et al. [13] carried out a techno-economic analysis of producing power and hydrogen from petcoke. For a petcoke feed rate of 4200 t/day, 437 MW of electricity and 12.87 tonne/hr of hydrogen (also equivalent to 437 MW of energy content) were produced resulting in a thermal efficiency of 25.6% on a lower heating value basis. A preliminary economic analysis was carried out by Jacob Consulting on a 4 Mt/yr petcoke plant that produces either methanol or hydrogen in which the net present value (NPV) was estimated as a function of oil and gas prices [9]. The study showed that there is a business case for using petcoke as a feedstock for fuel production. Similarly, the National Energy Technology Laboratory in the United States Department of Energy (NETL) performed a techno-economic study of converting petcoke to hydrogen, industrial grade steam, fuel gas, power, and liquid fuels [14]. They also concluded that there is a business case for petcoke conversion to fuels under the right market conditions. However, neither study looked at the potential environmental benefits of using waste petcoke as a resource, nor did they examine any potential synergies that could be exploited by combining petcoke with natural gas as feedstock.

Recently, Salkuyeh et al. [15], carried out an optimization study on a petcoke and natural gas polygeneration plant for the production of dimethyl ether (DME), methanol, olefins, and Fischer-Tropsch (FT) liquids. The result of the study showed that market prices strongly determined which of the possible products were the most economically optimal to produce. In addition, it was found that depending on market prices, the economically optimal polygeneration plant used either 20% petcoke (and 80% gas), or no petcoke at all, with the gas-only configuration strongly preferred with the market prices at the time of the study. However, the work only looked at economics and did not consider any potential environmental benefit by using waste petcoke as a resource instead of stockpiling. In addition, the study did not look at petcoke-only designs.

Therefore, this work focuses on the environmental benefits of using waste petcoke for FT liquids production. In this study, different petcoke conversion strategies are proposed as pathways by which petcoke can be converted to FT liquids. The design configurations evaluated are as follows: petcoke standalone gasification (PSG) in which petcoke is the only feedstock; petcoke integrated natural gas reforming (PG-INGR) which integrates petcoke gasification and natural gas reforming in the tubes of the gasifier's radiant syngas cooler; and petcoke external natural gas reforming (PG-ENGR), which uses petcoke gasification and natural gas reforming as separate units but blends their syngas products together. These designs were adopted from the work of Adams et al. [16].

The objective of this paper is to ascertain in detail the economic and environmental performance of the three proposed petcoke conversion strategies. A process flow diagram showing the different conversion strategies is shown in Fig. 1. A petcoke slurry is gasified in the presence of O_2 (99.5%) to produce syngas with low H_2/CO ratio. Depending on the configuration, either boiler feed water (BFW) or a natural gas/steam mixture is fed through the gasifier's radiant syngas cooler tubes (for natural gas, the tubes are packed with catalyst) providing the cooling duty required to cool the hot gasifier syngas and simultaneously either producing steam or syngas respectively in the process. This distinguishes the PSG and PG-ENGR configurations from the PG-INGR design as the hot gasifier syngas heat is used to drive the endothermic steam natural gas reforming process in PG-INGR instead of making high pressure steam (HPS) in the PSG and PG-ENGR designs.

The gasifier syngas is quenched and flashed to remove entrained impurities and contaminants. Water gas shift and carbonyl sulfide (COS) hydrolysis are employed to raise the H_2/CO ratio and convert COS to H_2S respectively. Natural gas derived syngas from the PG-INGR or PG-ENGR design is mixed with the shifted gasifier syngas and sent to the methyl di-ethanolamine (MDEA) based acid gas removal unit for H_2S and CO_2 removal. The absorbed H_2S is sent to the Claus unit for sulfur production while aqueous MDEA enriched with piperazine is used to capture CO_2 which is sent to the CO_2 compression unit for sequestration. A small amount of H_2 is extracted from the syngas via a pressure swing adsorber (PSA) unit for use in a downstream hydrocracker. The syngas is then sent to the FT reactor where it is converted to FT syncrude. The syncrude is distilled and hydrocracked to produce gasoline and diesel fractions. To promote the formation of liquids, 90% of the unconverted hydrocarbons are recycled back to the FT reactor while the remaining is combusted for HPS generation. For comparison, variants of each of these three designs were considered with no CO_2 capture and sequestration (CCS), resulting to a total of six designs considered in this analysis.

2. Methodology

2.1. Process simulation/assumptions

This paper considers the use of delayed coke produced in Alberta, Canada and conventional pipeline natural gas as the feedstocks that is to be converted to liquid fuels. Based on the NETL petcoke study [14], the petcoke feed rate is 219 t/hr (dry basis) with the natural gas feed rate sized according to the amount of radiant heat recovered in the gasifier that is available to drive the endothermic natural gas reforming reaction. The properties of the feedstock are shown in Table 1.

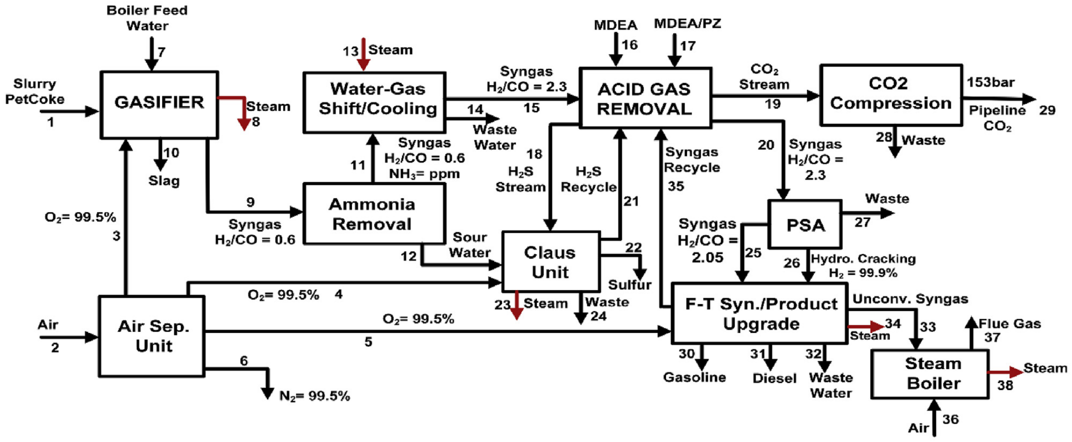
The simulation of the 3 petcoke conversion strategies was carried out in Aspen Plus v10 except for the MDEA based H_2S and CO_2 removal sections which were modeled in ProMax. The Peng-Robinson with Boston-Mathias (PR-BM) equation of state was used (which is consistent with our previous work [16]) with a few exceptions. The Amine package (in ProMax) was used for the ProMax MDEA model while the CO_2 compression unit in Aspen Plus used the Predictive Redlich-Soave-Kwong (PRSK) model which was shown in prior work to be superior at high pressures [18]. For the ammonia-water system, the PR-BM, PSRK, and the Electrolyte Non-random Two Liquid (ElectNRTL) model were evaluated and compared against the experimental work of Guillevic et al. [19] to determine the best candidate model for the NH_3-H_2O vapor-liquid equilibrium system as shown in Fig. 2. Both PSRK and PR-BM are about equally good; hence PR-BM was chosen to avoid model consistency issues with the rest of the flowsheet.

The Aspen Plus APV100 Pure 36 and Solids databases were employed for specifying the components: Conventional (CO, CO_2, H_2, O_2, H_2O, N_2, Ar, NH_3, H_2S, NO, NO_2, SO_2, SO_3, S_2, S_3, S_4, S_5, S_6, S_7, S_8, C_1-C_{30}), Solids (C, S), and non-conventionals (petcoke, slag, ash, char). Similar to Adams et al. [16], all $C_{30}+$ hydrocarbons were lumped as follows: C_{32} represents $C_{31}-C_{33}$, C_{36} represents $C_{34}-C_{39}$ while $C_{40}-C_{64}$ are pseudo-components specified to accurately represent the FT products using the normal boiling point, density, and molecular weights based on API gravity. Details of the models operating parameters and assumptions are shown in Table 2.

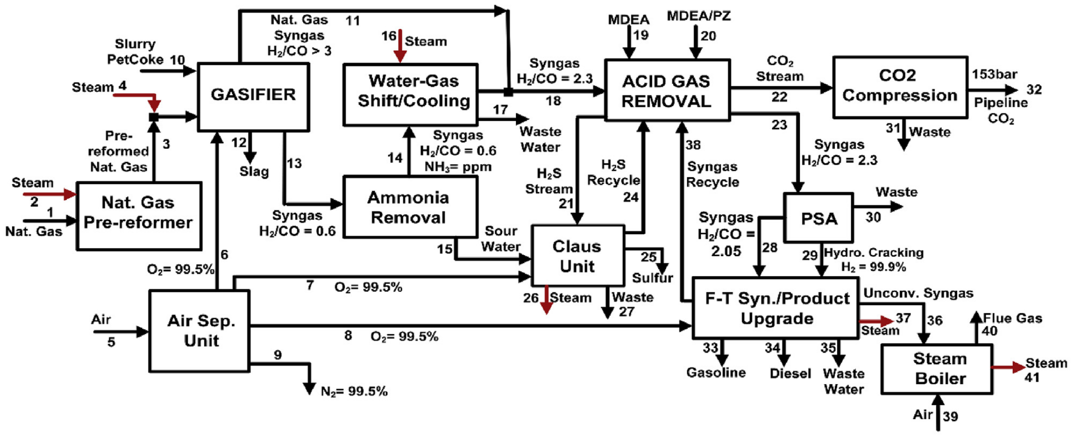
2.2. Air separation unit

Oxygen needed for the process is produced by compression, cooling, liquefaction and distillation of air in the overall cryogenic separation unit. This separation is enhanced by the boiling points difference which exists among air constituents (nitrogen, oxygen, carbon dioxide, argon, helium, neon, krypton and xenon).

PSG



PG-INGR



PG-ENGR

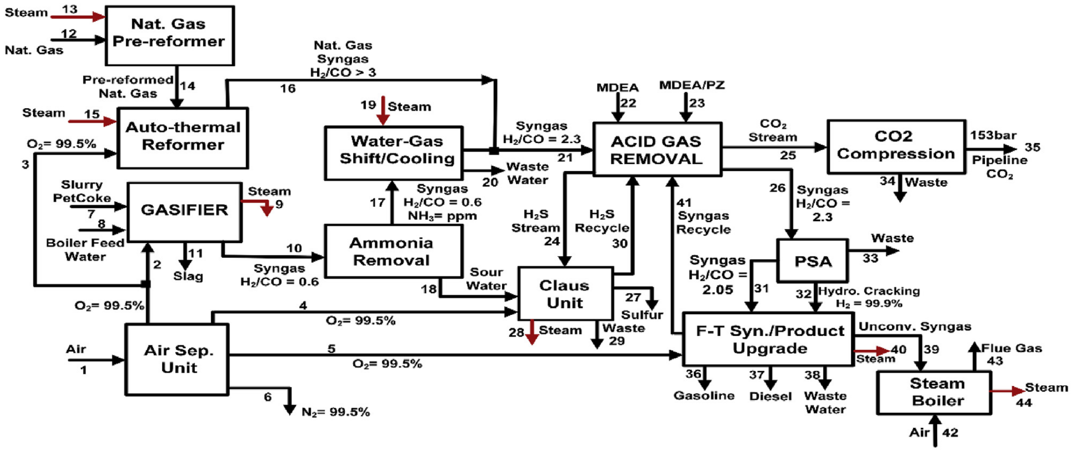


Fig. 1. Process flow diagrams for the three petcoke conversion to liquid fuels strategies.

Table 1
Delayed coke analysis [10] and Natural gas composition [17].

Delayed coke			
HHV (MJ/kg)	34.7		
Ultimate analysis (wt. % dry)			
C	84.9	Cl	0
H	3.9	Ash	3.1
N	1.3	O (diff)	0.8
S	6		
Proximate analysis (wt. %)			
Moisture	1.8	Fixed carbon	83.3
Volatile matter	11.9	Ash	3
Natural gas			
HHV (MJ/kg)	52.97		
Components (%mole)			
CH_4	93.9	CO_2	1.0
C_2H_6	3.2	C_4H_{10}	0.4
N_2	0.8	C_3H_6	0.7

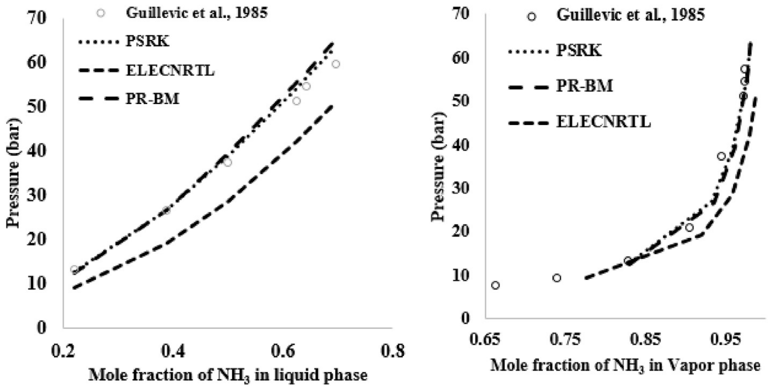


Fig. 2. Validation of vapor-liquid equilibrium mixtures of NH_3-H_2O system with three different models.

Atmospheric air is trapped and compressed to a discharge pressure of 1.3 MPa in a multi-stage with intercooler (at 31 °C) compressor allowing for removal of condensed vapor. In this paper, ASU separation coefficients were adopted from the work of [17] which was modeled in Aspen Plus using SEP and calculator blocks to compute and implement the mass balances that result in the production of oxygen at 99.5% purity. In this work, the ASU parasitic load which accounts for the sum total of the cryogenic section parasitic load and the boost compression of portions of the produced O_2 to the different pressure levels needed in the plant was estimated to be 0.41 MW/t/h of O_2.

2.3. Syngas production

2.3.1. PSG

Delayed petcoke delivered at the plant gate is ground and mixed with water to form slurry (H_2O: petcoke, 44 wt%/56 wt%) prior to being fed to the petcoke gasifier similar to the Wabash E-Gas gasifier [20] that processes petcoke. Gasification reaction comprises of pyrolysis, volatile combustion, char gasification, and sulfur reaction of which the product depends on the particular fuel characteristic. The slurry feed is gasified with oxygen (99.5% purity) at 1426 °C and 5.6 MPa to produce syngas consisting primarily of H_2, CO, CO_2, and other impurities [17,30]. To accurately represent the overall gasification process, the pyrolysis (breakdown) of the solid fuel to elemental species is first modeled as petcoke decomposition occurring at 550 °C [31] in an RYield reactor using calculator block to estimate the components yields which is based on fuel composition. Then followed by the actual gasification reactions such as volatile combustion, char gasification, and sulfur reactions in the petcoke gasifier modeled in Aspen Plus using RGibbs reactor which follows a restricted chemical equilibrium approach to produce syngas.

Oxygen is fed to the reactor in such a way that the desired reactor temperature is maintained during the gasification process. The heat of fusion of ash (230 kJ/kg) [32] and heat loss to the environment (assumed to be 1% of $HHV_{petcoke}$) during gasification were considered for the energy balance of the gasifier. Boiler feed water (BFW) is used to provide the cooling duty required by the hot gasifier syngas cooling it to 760 °C in the radiant syngas cooler (RSC) producing HPS [20,33]. Conversion of carbon in petcoke was assumed to be 99% similar to the petcoke gasification test of Wabash River [20]. The unconverted carbon in the feed was considered to be ash in addition to trace metals such as vanadium and nickel which exists the gasifier as slag [31]. To remove the slag entrained in the syngas, the gas is passed through a water-quench pool at an adiabatic saturation temperature of about 200 °C. Ammonia removal from syngas which deactivates the FT catalyst [34] was carried out based its high solubility in the NH_3—H_2O system reducing it to 10 ppm limit [35]. The NH_3 rich water termed “sour water” is sent to the Claus unit for NH_3 destruction [24].

Table 2
Model operating parameters and assumptions.

Unit	Parameters	Ref
Main design parameters		
ASU	Oxygen purity (99.5%) @ 32 °C, P = 13 bar	[18]
Gasifier	Slurry water/petcoke (44w%/56w%) Two train E-Gas Gasifier Exit conditions: T = 1426 °C, P = 55 bar	[20]
Water Gas Shift	Low Temp adiabatic reactor, T: 207 °C High Temp adiabatic reactor, T: 425 °C COS hydrolysis adiabatic reactor T:177 °C, Conversion $\gg$ 99%	[21,22]
Acid Gas Removal	MDEA H_2S removal: T = 40 °C, P = 5.5 bar MDEA/piperazine CO_2 removal: T = 40 °C, P = 30 bar	[23]
CO_2 Compression	Multistage compressor with intercoolers CO_2 Purity (99.5%) T = 26 °C, P = 153 bar	[17]
Sulfur Recovery (Claus)	Split flow (H_2S > 15%), Furnace Temp.: 950 °C	[24]
PSA	Hydrogen purity: 99.9%	
F-T/Product Upgrade	F-T Slurry reactor: T = 220 °C, P = 30 bar CO conversion: 80% Product ASTM spec (95% vol): gasoline = 170 °C, diesel = 340 °C	[16,25,26]
Cooling tower	Wet bulb temp: 11 °C, Approach temp: 5 °C, cooling water range 11 °C Cooling water inlet: 16 °C	[17]
Assumptions		**Ref**
Min temperature approach in heat exchanger	5 °C	[18]
Low pressure steam	4 bar, 204 °C	[27]
Medium pressure steam	12 bar, 300 °C	[27]
High pressure steam	50 bar, 480 °C	[27]
Fired heat	1000 °C	[28]
Chilled water	4 °C	[29]
Isentropic efficiency in compressors	80%	[18]
Mechanical efficiency in compressors	100%	[18]
Max pressure ratio in compressors	5	[18]
Pump efficiency	80%	[18]

2.3.2. *Natural gas reforming*

Pipeline natural gas is delivered to the plant gate at 30 °C and 30 bar with the composition as shown in Table 1. Due to the presence of higher hydrocarbons, the gas is adiabatically pre-reformed at 450 °C to achieve up to 99% of all >CH_4 hydrocarbons [36]. This design applies to both the PG-INGR and PG-ENGR configurations. Note that for the PG-INGR configuration, because of the high temperatures inside of the gasifier shell, the pre-reforming step must occur external to the PG-INGR where the methane is reformed [37].

2.3.2.1. PG-INGR configuration. Steam methane reforming is used to provide the cooling duty required by the hot gasifier syngas. This is achieved by sending the pre-reformed natural gas and steam through the RSC tubes packed with alumina catalyst thereby reforming the natural gas for additional syngas production. Gasifier syngas leaves at 760 °C which is equivalent to 216 MW cooling duty. To determine the natural gas and steam feed rate (for at least 80% methane conversion) that will provide the required cooling duty, a first principles model of an integrated petcoke gasification and steam methane reformer based on the work of Ghouse et al. [37] was used in gProms. The model is multi-scale and considers spatial gradients temperature, concentration, and pressure of the gases in both sides of the tubes. It also models the effects of diffusion within the catalyst particles themselves to the millimeter scale, and is approximately 100,000 equations in size (see Ref. [37] for details). In addition to methane conversion, the tube exit temperature, pressure drop, and steam conversion were also determined with this model. The tube syngas has a H_2/CO ratio > 3 which is mixed with the gasifier syngas for downstream conversion.

2.3.2.2. PG-ENGR configuration. Similar to the work of Salkuyeh et al. [15], this design explores the performance of combining petcoke and natural gas as feedstock in the conversion strategies by reforming natural gas in an auto-thermal reformer. For comparison, the same amount of pre-reformed natural gas is fed to an auto-thermal reformer operating at 950 °C and 30 bar. Oxygen is used for in-situ oxidation of the methane thereby providing the heat requirement of the process while the steam to carbon ratio was varied to obtain the desired H_2/CO ratio > 3. The syngas generated in this process is mixed with the gasifier syngas for subsequent downstream conversion to FT liquids.

2.4. *Syngas shifting*

Water gas shift (WGS) is employed to convert the excess CO in the petcoke derived syngas to achieve the desired H_2/CO ratio. Typical of industrial processes, both the high temperature water gas shift (HTWGS) and low temperature water gas shift (LTWGS) reactors operating adiabatically were used in series due to equilibrium limitations of the HTWGS [38]. The HTWGS operates at about 425 °C in the presence of chromium or copper promoted iron-based catalysts followed by the LTWGS reactor operating at 260 °C in the presence of copper-zinc-aluminum completing the shift process [21] to the desired H_2/CO ratio of 2.3. The excess H_2 is used in the hydrocracking unit. In addition to the CO conversion in the WGS reactors, COS conversion to H_2S also takes place simultaneously. Both reactors were modeled in Aspen Plus using an equilibrium model (REquil) with these reactions:

$$CO + H_2O \leftrightarrows H_2 + CO_2 \tag{1}$$

$$COS + H_2O \leftrightarrows H_2S + CO_2 \tag{2}$$

To achieve up to 99% of COS conversion, equilibrium catalytic hydrolysis of COS in the presence of activated alumina catalyst was employed [22]. Finally, the syngas is cooled to 40 °C and flashed to remove waste water while the syngas is sent to the acid gas removal unit.

2.5. *Acid gas removal*

Acid gas removal was simulated in ProMax using MDEA to remove H_2S and CO_2 from the syngas. Syngas is fed through the bottom of the H_2S absorber operating at 40 °C in a counter-current fashion with the MDEA/H_2O (50%:50%) solvent [23,39]. Although H_2S and CO_2 are highly soluble in MDEA, the solubility of H_2S proceeds at a very fast rate compared to CO_2 [40] which ensures minimal pickup of CO_2 in the H_2S absorber. The H_2S absorber was designed to achieve 98% H_2S removal efficiency with a solvent to feed ratio of 1.85. Syngas exiting the top of the absorber is cooled, flashed to remove some of the entrained water, and sent to the CO_2 absorber unit while the bottoms product (rich MDEA solution) exiting the bottom of the absorber is regenerated in the H_2S stripping column operating at 2 bar. Exiting the top of the H_2S stripper is a stream containing 15% H_2S which is sent to the Claus unit for split flow sulfur recovery process [24] while the bottoms stream made up of the regenerated solvent is pumped back to the top of the H_2S absorber.

In the CO_2 absorber, the capture of CO_2 from the syngas is promoted by the aid of piperazine [41,42] which enhances the overall absorption of CO_2 given its slow reactivity in MDEA [23]. A solvent mixture of (50%wt:45%wt:5%wt) H_2O/MDEA/piperazine was employed [41]. Apart from the use of piperazine, the process is similar to the H_2S absorption process. The absorber was designed to capture 90% CO_2 which is typical for solvent based carbon capture [43,44] with a solvent to feed ratio of 2.98. The syngas exiting the CO_2 absorber is sent through the PSA to the FT unit while the CO_2 stream is sent to the CO_2 compression unit.

2.6. *Claus process*

Hydrogen sulfide from the AGU is catalytically converted to elemental sulfur in the Claus process. The basic reactions comprise the partial oxidation of H_2S to produce SO_2 followed by the reaction of the unconverted H_2S with SO_2 as shown in the reactions:

$$H_2S + 3/2O_2 \rightarrow SO_2 + H_2O \tag{3}$$

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \tag{4}$$

Combustion of acid gas and sour water in the presence of limited oxygen in a Claus furnace takes place at 950 °C [24] to generate gas mixture with the desired stoichiometric coefficient of 2:1 for H_2S and SO_2 respectively for subsequent conversion to sulfur and water [45,46]. Some elemental sulfur is produced at the furnace with the sulfur reactions modeled as an equilibrium reaction with temperature approach. Exiting the furnace is a hot stream containing predominantly elemental sulfur that is cooled in the waste heat boiler (WHB) recovering heat that is used for HPS generation [45]. The stream leaving the WHB is condensed and reheated to 210 °C upstream the catalytic reactors [24]. Two stage catalytic reactors with intermediate condensers and heaters were used [24,45] for this process achieving a sulfur recovery of 96% [47]. The recovered sulfur is cooled and stored in sulfur pit for subsequent sale while the unconverted H_2S is recycled back to the MDEA unit.

2.7. *Pressure swing adsorption*

Prior to the FT reactor, PSA is used to recover 99.99% pure hydrogen from the syngas stream. Since hydrogen is the desired component, adsorbent with low binding force with hydrogen due to its low polarity and very high volatile is used. Detailed modeling of the PSA is not within the scope of this work and was represented using a SEP block in Aspen Plus by setting the hydrogen recovery to 99.99%.

2.8. *Fischer-Tropsch synthesis/product upgrade*

Liquid fuels production takes place in the low temperature FT slurry reactor in the presence of cobalt catalyst. The choice of reactor, temperature and catalyst is to promote the formation of diesel fractions of the fuel. Syngas entering the FT slurry reactor with the desired H_2 to CO ratio of 2.05 is raised to 240 °C and 30 bar with the reactions proceeding as:

$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O \tag{5}$$

$$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O \tag{6}$$

$$nCO + 2nH_2 \rightarrow C_nH_{2n+1}\,OH + (n-1)H_2O \tag{7}$$

A single pass CO conversion of 80% was assumed which is typical of the slurry phase reactors [25]. Theoretically, the production of diesel fraction of liquid fuels is promoted by higher α value. Since values for industrial FT reactors are characterized between 0.65 and 0.95 [48], a high value (0.92) was chosen. The product distribution is based on the work of Adams et al. [16]. The syncrude produced in the FT reactor is cooled, decanted to remove water, and sent to the product upgrading unit. For brevity, the detailed modeling of the hydrocracking of heavy hydrocarbons, product upgrade, and product distribution to produce gasoline and diesel can be found in Adams et al. [16]. In order to maximize the production of liquid fuels, 90% of the unconverted hydrocarbons are recycled to the FT reactor via an auto-thermal reactor which reforms the unconverted hydrocarbons to H_2 and CO while the remaining 10% was used for HPS generation.

2.9. *Heat integration (utilities and cooling tower system)*

Plant wide utility management was designed and optimized using Aspen Energy Analyzer (AEA) to maximize heat recovery; thus, minimizing energy requirement (MER). The heat exchanger network that meets the MER was designed using pinch analysis. All process streams with their process conditions were exported from Aspen Plus to AEA. Assuming a minimum approach temperature (ΔT_{min}) of 5 °C [18,27], the composite curves (CC) and grand composite curves (GCC) were constructed as depicted in Fig. 3 showing the pinch temperatures and maximum possible heat that can be recovered by process to process heat exchange.

The conditions of the utility streams used for the design are shown in Table 2 with the detailed hot and cold stream temperatures (and their corresponding mass flow rate, enthalpy, etc.) for each of the designs provided in the supplementary document. For the design of the HEN, the utility allocation method employed was the grand composite curve (GCC) utility allocation method

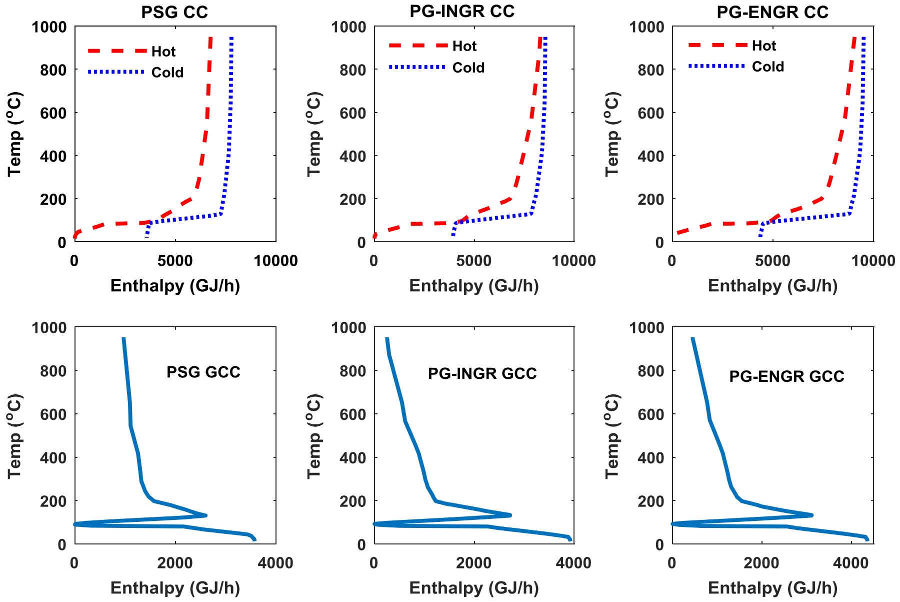


Fig. 3. Composite and Grand composite curves for the three petcoke conversion strategies at $\Delta T_{min} = 5\,^{\circ}C$.

proposed by Linnhoff et al., [49]. In this approach, the cheapest utility that satisfies the target temperature requirements is chosen first so as to minimize operating cost. Hence, the objective function of the HEN design is to minimize the total annualized cost (TAC) by varying the stream matches, their corresponding heat exchanger loads, and any stream splits giving rise to a mixed integer linear program (MILP). AEA does not guarantee a global optimal solution but proposes multiple near-optimal designs of the HEN. The design with the smallest TAC was chosen as the best candidate design for each of the configuration strategies. A visual representation of the overall HEN designs can also be found in the supplementary document. In addition, the reader can download the AEA file for further details at http://PSEcommunity.org/LAPSE:2018.0148.

The cooling water requirement of the process was designed using a mechanical draft evaporative cooling tower system with an approach temperature of 5 °C and cooling range of 11 °C [17]. The estimation of the amount of cooling tower makeup followed a correlation in Ref. [50] with cycles of concentration, and evaporative and drift losses of 5, 0.8%, and 0.001% respectively. The cooling tower pump and the fan together accounts for the tower electrical power consumption, which was calculated using correlations from Turton et al. [50], using a pump efficiency of 80% and pressure drop of 2.6 bar.

2.10. *Techno-economic analysis*

A techno-economic analysis (TEA) of the 3 petcoke conversion strategies to liquid fuels was conducted to determine the most profitable design. Detailed economic assumptions are shown in Table 3 which was made to be consistent with the NETL petcoke gasification study [14]. The discounted cash flow rate of return approach was used to estimate the net present value (NPV). Since diesel is the main product of the process, the minimum diesel selling price (MDSP) was also calculated as the selling price which results in a NPV of zero.

Table 3
Economic assumptions.

Parameter	Value	Ref
Plant life (yrs)	30	[16]
Construction period (yrs)	2.5	
Plant loan (yrs)	30	
Plant loan interests	9.50%	[51]
Debit/Equity (%)	80/20	[14]
Tax Rate	40	[51]
Rate of Return	12%	[14]
Depreciation Method	MACRS	
Working capital	5% TPC	[52]
Length of start-up	20	
Operating Hours	8000	

With the aid of the mass and energy balance, the equipment costs for the three conversion strategies were estimated using a combination of literature and Aspen Process Economic Analyzer (APEA v10) except the gasifier of the PG-INGR configuration. Because no economic data exist for the integrated gasifier (since it has not been commercialized), it was assumed that the integrated gasifier costs 50% more than a gasifier with a typical radiant syngas cooler of the same capacity as reported by the NETL [17]. This parameter was subjected to a sensitivity analysis to ascertain its effect on the NPV. Plant wide heat exchanger costs were obtained from the AEA results. All estimated equipment costs were scaled up to US$2017 using the chemical engineering plant cost indices [53]. Details of the capital cost estimation can be found in the attached supplementary information. Variable operating costs (feedstock, catalysts, utility) and product prices were obtained from literature reports and market prices respectively which were scaled to $2017 while the fixed operating costs (labor, maintenance, and overhead) were calculated using the method given by Seider et al. [29]. The variable and fixed operating costs are detailed in Table 4.

Table 4
Fixed and Variable operating costs based on market and literature data.

Fixed costs (Labor, Maintenance, and Overheads)		Ref
Direct wages and benefits (DW&B)	32 operators/shift	[29]
Direct salaries and benefits	15% of DW&B	[29]
Operating supplies and services	6% of DW&B	[29]
Tech. assistance to manufacturing	$60,000 base for 5 shifts	[29]
Control laboratory	$65,000 base for 5 shifts	[29]
Maintenance, wages, and benefits (MW&B)	4.5% of TDEC	[29]
Salaries, wages, and benefits (SW&B)	25% of MW&B	[29]
Materials and services	100% of MW&B	[29]
Maintenance overhead (M&O)	25% of MW&B	[29]
Operating Overhead	22.8% of M&O-SW&B	[29]
Property Insur. & Tax	2% of TDEC	[29]
Feedstock, product, and byproducts prices		
Petcoke (Feedcost)	$0.00/tonne	[14]
Natural gas	$2.43/MMBtu	[71]
Sulfur price	$70/ton	[54]
Gasoline	$1.826/gal	[55]
Diesel	$1.852/gal	[56]
Utility		
Cooling tower Water	$0.0148/tonne	[50]
Chilling Water	$4.00/GJ	[29]
Boiler Feed Water	$0.5/tonne	[29]
Electricity	$38/MWh	[72]
LP Steam	$7.78/GJ	[50]
MP Steam	$8.22/GJ	[50]
HP Steam	$9.83/GJ	[50]
Fired heat	$7.5/GJ	[50]
Solvents, catalysts & wastes		
Waste Water Treatment	$0.528/tonne	[52]
MDEA Price	$244/tonne	[57]
Piperazine	$244/tonne	Assumed
Ash	$15.45/ton	[17]
WGS Catalyst	$63.889/kg	[17]
Claus Catalyst	$125/ft^3	[17]
COS Catalyst	$2308.4/m^3	[17]
FT Catalyst	$35/kg	[58]
Product upgrade Catalyst	$56.36/kg	[59]
CO_2 Emission	$50/tonne	[16]

3. Results and discussion

3.1. Process simulation

The converged Aspen Plus simulation files for all six cases are available for download on the digital archive at PSEcommunity.org.[1] The results of the 6 petcoke conversion strategies (with CCS and w/o CCS) are briefly summarized in Table 5 detailing the feed rates, total electricity consumption, fuels production rates, byproduct rate, and cradle to plant exit life cycle GHG emissions. Also, feed carbon, fuel, and energy efficiencies were computed. It is noteworthy to observe the amount of natural gas feed to the PG-INGR and PG-ENGR designs. This is based on the 216 MW of heat recovered in the gasifier radiant cooler which was used to drive the natural gas to 80% conversion.

Comparing the three designs with CCS, the PG-ENGR design consumed the highest amount of electricity, 36% more than PGS and 16% more than PG-INGR. This high amount of power consumption in the PG-ENGR design is because of the high parasitic load of the ASU in providing the oxygen needed to drive the autothermal reformer. Without CCS, there is an 18%, 12%, and 14% reduction in electricity demand for the PGS, PG-INGR, and PG-ENGR designs respectively when compared to the CCS plant. Liquid fuels production for the PG-INGR and PG-ENGR conversion strategies that combined petcoke and natural gas are 65% and 46% respectively higher than the PGS which converts only petcoke, due in large part to the much larger amount of total feedstock used. However, PG-INGR produces 12% more liquid fuels than PG-ENGR even though they both use the same amount of feedstock, signifying that the PG-INGR design has much improved conversion capability.

3.2. Process emissions

3.2.1. CO_2 capture and emissions

The direct and indirect CO_2 emissions of the configuration for the CCS and non-CCS enabled scenarios are shown in Fig. 4. The direct emissions consist of all the process GHG emissions from the plant entry to the plant exit while the indirect emissions accounts for all cradle to plant entry GHG emissions. The electricity emission used in this study is the average Ontario electricity mix emission of 52.76 gCO_2eq/kWh [60]. GHG emissions for natural gas extraction and transportation, and utility emissions were obtained from NETL [61] and EPA [62] respectively. In this study, the indirect emissions of petcoke production was taken to be zero which is reasonable as it is an undesired waste product of refinery operation (one does not refine oil to get the petcoke); thus, all petroleum extraction and refining emissions are attributed to the useful refinery products instead.

Fig. 4 shows a higher indirect emission of the CCS plants compared to their non-CCS counterpart due to the parasitic CCS technology. On an absolute basis, the PG-INGR design has 59% and 19% more direct emissions than the PSG and PG-ENGR designs (see Table 5). When expressed per GJ of liquids produced, the CCS plants have almost the same amount of direct emission whereas the

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[1] The permanent link to the files is: http://PSEcommunity.org/LAPSE:2018.0148.

Table 5
Summary of the different design performance.

	PSG	PSG	PG-INGR	PG-INGR	PG-ENGR	PG-ENGR
CCS Enabled	Yes	No	Yes	No	Yes	No
Petcoke Feed rate (tonnes/h)	218.7	218.7	218.7	218.7	218.7	218.7
Gasifier Radiant Heat Recovered (MW)	216	216	216	216	216	216
Natural Gas (tonnes/hr)	–	–	52.3	52.3	52.3	52.3
Total Electricity consumed (MW)	232.2	189.4	272.7	239.2	315.0	270.5
Fuel Efficiency (HHV%)	43.4	43.4	51.9	51.9	46.2	46.2
Energy Efficiency (HHV%)	33.4	36.4	42.6	44.6	36.6	37.9
Carbon Efficiency (%)	32.2	32.2	43.7	43.7	38.9	38.9
Gasoline produced (ML/yr)	232.2	232.2	386.8	386.8	344.1	344.1
Distillate produced (ML/yr)	627.3	627.3	1025.9	1025.9	914.4	914.4
Sulfur produced (ktonnes/yr)	99.8	99.8	99.6	99.6	99.1	99.1
CO_2 sequestered (Mtonnes/yr)	3.5	–	3.4	–	3.7	–
Direct GHG emitted (MtonnesCO_2eq/yr)	0.14	3.58	0.22	3.58	0.18	3.91
Indirect GHG emitted (MtonnesCO_2eq/yr)	0.36	0.002	0.79	0.36	0.42	0.26
Direct GHG emitted (kgCO_2eq/GJ)	5.17	135.82	5.03	82.81	4.76	101.5
Indirect GHG emitted (kgCO_2eq/GJ)	13.54	0.09	18.29	8.42	10.79	6.67
Total GHG emission (kgCO_2eq/GJ)	18.72	135.91	23.32	91.23	15.55	108.17

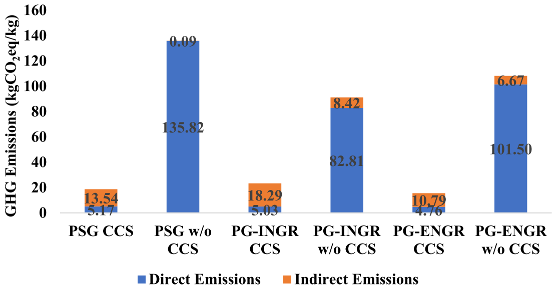

Fig. 4. Cradle-To-Product GHG emissions for the different designs.

PG-ENGR has approximately 20–41% lower indirect emissions compared to the PSG and PG-INGR designs. Similarly, total cradle to plant exit gate GHG emissions for PG-ENGR are 17–33% lower than the PSG and PG-INGR designs. Without CCS, although there is a significant drop in indirect emissions across the designs due to less parasitic load, the direct emissions of the PSG, PG-INGR, and PG-ENGR designs are 16–26 times higher than their CCS-enabled counterparts. Overall, the PG-INGR design emits the least total life cycle CO_2 even when operated without CCS.

3.2.2. *Cost of CO_2 avoided*

An important metric for comparing different designs and processes for the purpose of capturing or reducing CO_2 emissions compared to a reference plant (typically a plant that represents the status quo without carbon capture technology) is the cost of CO_2 avoided (CCA) [44]. For this study, an oil sands crude oil refinery is used as the reference plant as it produces the same product. Therefore, the CCA is defined as:

$$CCA = \frac{\left(TPC_{CCS\_plant} - TPC_{Refinery}\right)}{\left(GHG_{Refinery} - GHG_{CCS\_plant}\right)} \tag{8}$$

where TPC_{CCS_plant} and GHG_{CCS_plant} are total product cost (TPC in \$/GJ) and total cradle to plant exit gate emissions (tonneCO_2e/GJ) of a liquid fuels plant with CCS respectively while $TPC_{Refinery}$ and $GHG_{Refinery}$ are total product cost (TPC in \$/GJ) and total cradle to plant gate exit emissions (tonneCO_2e/GJ) of a refinery without CCS respectively.

The refinery cradle to plant exit gate GHG emissions used in this work is 30.38 kgCO_2eq/GJ which is consistent with that from GREET model [63] and the Lattanzio [64]. This included the total direct and indirect emissions of oil sands extraction, transportation to refinery, and emissions for production of 1 GJ of diesel (62%) and gasoline (38%) respectively. The GHG emissions computed followed the International Panel on Climate Change (IPCC) 100-year metric. Considering only diesel and gasoline refinery emissions helps to ensure product emission consistency. To calculate the TPC, the capital investment (M\$) was annualized using the Smith et al. [65] annualization factor (AF):

$$AF = \frac{i(1+i)^n}{(1+i)^n - 1} \tag{9}$$

where i is the rate of return (%) and n is the plant life (yrs).

The annualized capital investment (M\$/yr) was added to the plants' annual operating cost (M\$/yr), divided by the annual production capacity (APC) to obtain the TPC of the process (in \$/GJ) as shown as:

$$TPC_{CCS\_plant}\left(\frac{\$}{GJ}\right) = \left[TCI*AF\left(\frac{\$}{yr}\right) + AOC\left(\frac{\$}{yr}\right)\right] \div APC\left(\frac{GJ}{yr}\right) \tag{10}$$

Total product cost of the refinery was estimated using the reported wholesale prices (WP) of diesel [56] and gasoline [55] in the US. Diesel and gasoline were assumed to be the only products of the refinery accounting for 62% and 38% respectively which is similar to the fuel fractions (FF) obtained in this work. Since the reported refiner's plant gate prices for the products usually includes refinery margins (RM), which have been reported to be up to \$5.5/bbl based on the current crude oil price [66], the margin was factored into the refiner's WP as shown in equation (11) to obtain a refinery total product cost of \$14.72/GJ which was used as the TPC of the refinery.

$$\begin{aligned} TPC_{refinery}\left(\frac{\$}{GJ}\right) = \Bigg[&\left(WP_{diesel}\left(\frac{\$}{gal}\right) \div HHV_{diesel}\left(\frac{GJ}{gal}\right) * FF_{diesel}\right) \\ &+ \left(WP_{gasoline}\left(\frac{\$}{gal}\right) \div HHV_{gasoline}\left(\frac{GJ}{gal}\right) * FF_{gasoline}\right) \\ &\times \Bigg] * RM \end{aligned} \tag{11}$$

Table 6 shows the calculated CCA in \$/tonneCO_2eq for the

Table 6
Cost of CO_2 Avoided Calculation for the three configurations with CCS enabled.

	PSG	PG-INGR	PG-ENGR
CCS-Enabled	Yes	Yes	Yes
Total capital Cost (M$)	1116	1382	1370
Annualized capital Cost (M$/yr)	294	365	361
Operating Cost (M$/yr)	235	345	315
Total Product (MGJ/yr)	26.4	43.3	38.5
Total Product cost ($/GJ)	20.1	16.4	17.6
GHG (kgCO_2eq/GJ)	18.72	23.32	15.55
CCA ($/tonne$CO_2$eq)	459	237	193

different configurations. Considering the high cost ($/GJ) and emissions of the PGS design, it clearly is not a good choice for environmental purposes when compared to the petcoke and natural gas designs as its CCA is approximately 1.9–2.4 times that of the PG-INGR and PG-ENGR designs, respectively. Also, the CCA of the PG-INGR design is 1.2 times that of the PG-ENGR design. Therefore, the external reforming strategy is clearly the best option in terms of environmental emissions.

3.3. Process efficiencies

3.3.1. Carbon efficiency

To further study the performance of the each of the design configurations, the carbon efficiency, which is the percentage of carbon in feedstock which ends as useful product, was evaluated. The carbon efficiency (η_{carbon}) is defined as:

$$\eta_{carbon} = \frac{Diesel_{carbon} + Gasoline_{carbon}}{Fuel_{carbon}} \tag{12}$$

where $Diesel_{carbon}$, $Gasoline_{carbon}$, and $Fuel_{carbon}$ are the mass of carbon atoms in diesel product, gasoline product, and fuels (petcoke only or petcoke and natural gas) depending on the design employed. Fig. 5 shows the percentages of carbon in product, carbon sequestered, and carbon emitted. The PG-INGR configuration (with or without CCS) has the highest carbon efficiency of 43.7% which is 11.5 and 4.80 percentage-points larger compared to the PSG and PG-ENGR designs respectively.

3.3.2. Fuel and energy efficiencies

The efficiency of the design to convert the fuel to desirable product is defined as fuel efficiency (η_{fuel}) which is given as:

$$\eta_{fuel} = \frac{Diesel_{HHV} + Gasoline_{HHV}}{Fuel_{HHV}} \tag{13}$$

The efficiency of fuels conversion which takes into consideration all the total energy input to the system is defined as energy efficiency η_{energy} which is given as:

$$\eta_{energy} = \frac{Diesel_{HHV} + Gasoline_{HHV}}{Fuel_{HHV} + Electricity\ consumed + Utilites\ consumed} \tag{14}$$

where $Diesel_{HHV}$, $Gasoline_{HHV}$, and $Fuel_{HHV}$ are the high heating values (HHV) of diesel product, gasoline product, and fuels (petcoke only or petcoke and natural gas) depending on the design employed.

Fig. 6 shows the fuel and energy efficiencies in HHV% for the different configurations with CCS and w/o CCS. It can be seen that for 1 MJ of petcoke, 0.43 MJ of FT fuel is produced for the PSG design showing a significant amount of energy that could be extracted from petcoke instead of stockpiling it as routinely done in Canada [9,67]. This would offset the extra amount of crude oil extracted to met liquid fuels demand since petcoke, the solid waste of crude processing, can be further converted to produce more transportation fuels.

Posing environmental concerns due to the high carbon emissions of the PSG design, this research work explores in a more rigorous fashion other technical and economical viable ways of converting petcoke with minimal environmental impacts. Combining natural gas with petcoke, the fuel efficiency increased to 51.9% and 46.2% for the PG-INGR and PG-ENGR configurations respectively which is of huge significance in fuels production. Energy efficiency for the CCS plants dropped by 10%, 9.3%, and 9.6% points for the PSG, PG-INGR, and PG-ENGR designs respectively showing the extra energy input to the plants. Without CCS, the fuel efficiency remains same but increases for the energy efficiency due to the reduced amount of thermal requirement when the plant operates without CCS. Overall, the PG-INGR configuration with an energy efficiency of approximately 42.6% (with CCS) shows a design that is comparable with commercial petcoke plant [20]; thus, exhibiting a sign of competitiveness.

3.4. Economic analysis

The profitability assessment of the petcoke configuration strategies was carried out and the results summarized in Table 7 which

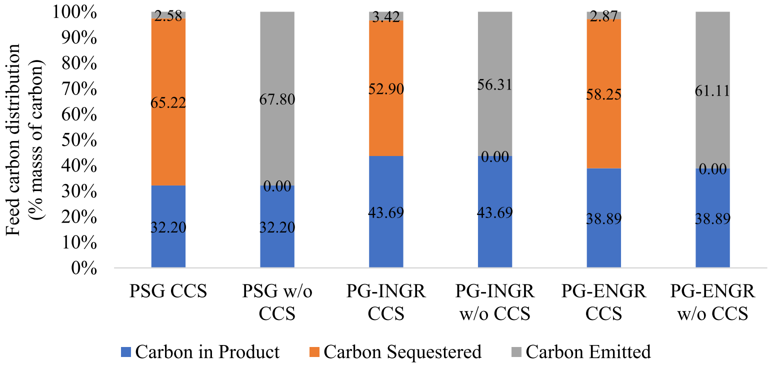

Fig. 5. Carbon distribution for each of the design configurations.

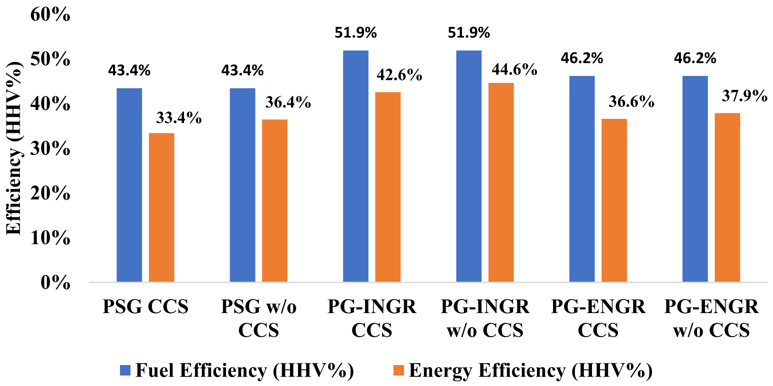

Fig. 6. Fuel and energy efficiencies for each of the design configurations.

Table 7
Economic summary for different configurations.

Scenario						
Design configuration	PSG	PSG	PG-INGR	PG-INGR	PG-ENGR	PG-ENGR
CCS enabled	Yes	No	Yes	No	Yes	No
Capital cost by section (M$)						
Air separation unit	68.6	68.6	70.9	70.9	77.3	77.3
Solid handling	3.1	3.1	3.1	3.1	3.1	3.1
Slurry prep & feed	34.2	34.2	34.2	34.2	34.2	34.2
Gasification	180.4	180.4	180.4	180.4	180.4	180.4
Ash/slag silos	0.3	0.3	0.3	0.3	0.3	0.3
Water gas shift	33.7	33.6	34.1	34.1	34.6	34.6
Pre-reformer	–	–	9.1	9.1	9.1	218
Natural gas reformer	–	–	90.2	90.2	44.6	77.4
Acid gas removal	169.9	72.2	212.7	86.9	226.8	101.7
CO_2 compression	9.4	–	9.3	–	9.7	–
Claus unit	48.8	48.8	48.6	48.6	51.3	51.3
Pressure swing adsorption	11.6	11.6	15.7	15.7	14.6	14.6
Fischer-Tropsch synthesis	131.3	131.3	208.6	208.6	157.7	157.7
Cooling tower	13.7	12	10.3	80.0	15.3	10.8
Heat exchanger network/steam system	164.7	139.7	149.4	55.0	207.9	241.1
Cost breakdown at 85% capacity factor						
Total capital investment (M$)	1116.8	944.8	1382.4	1184.9	1370.0	1162.8
Annual operating cost (M$/yr)	246.8	371.4	361.5	476.0	335.4	487.8
Total labour cost (M$/yr)	14.7	14.7	14.7	14.7	14.7	14.7
Total maintenance cost (M$/yr)	90.0	76.2	111.4	95.5	110.4	93.7
Operating overhead (M$/yr)	14.2	12.5	16.9	14.9	16.7	14.7
Property insurance & tax (M$/y)	17.4	14.7	21.5	18.5	21.3	18.1
Petcoke cost (M$/yr)	0.00	0.00	0.00	0.00	0.00	0.00
Natural gas cost (M$/yr)	–	–	52.3	52.3	52.3	52.3
Total utility costs (M$/yr)	88.4	48	127	78.7	95.6	70.1
Sulfur sales (M$/yr)	9.9	9.9	9.9	9.9	9.8	9.8
Gasoline sales (M$/yr)	97.9	97.9	162.8	162.8	145.0	145.0
Diesel sales (M$/yr)	268.2	268.2	439.6	439.6	390.9	390.9
Gross earnings (M$/yr)	375.9	375.9	612.3	612.3	545.7	545.7
Net present value (M$)	74.3	−588.7	714.2	294.1	489.2	−212.5

shows the detailed cost breakdown of the total capital investment (TCI), operating costs, and product revenues. The results presented in this table are for the petcoke feed capacity of 219 tonnes/hr which is consistent with the work of NETL [14].

One of the reasons why the PG-INGR and PG-ENGR designs appears much more profitable than the PSG design in Table 7 is from economy of scale, since the designs using natural gas use considerably more feedstock. Therefore, the profitability analysis was repeated such that the six designs were scaled to have the same thermal input as the PSG design which is equivalent to a thermal input of 2108 MW (HHV), as summarized in Table 8. As a result, these designs all had approximately the same capital cost as well (approximately $1 billion), and so are suitable for comparison on the basis of similar capital investment.

When comparing the plants in this way, the combined petcoke and natural gas designs still have higher product yields, and higher NPVs, but a lower GHG emissions per product delivered, and lower CCAs for the PG-ENGR design compared to the petcoke only design, showing that integrating natural gas can be superior in some of the most important metrics. Furthermore, PG-INGR has 12% more product yield than PG-ENGR, which clearly attests to a key performance improvement of the integrated design. However, it was observed that the PSG and PG-ENGR designs are similar in terms of absolute emissions rates and power consumption.

Table 8
Economic summary for the scaled designs for the 6 different configurations.

	PSG	PSG	PG-INGR	PG-INGR	PG-ENGR	PG-ENGR
CCS-Enabled	Yes	No	Yes	No	Yes	No
Petcoke rate (tonnes/h)	218.7	218.7	159.2	159.2	159.2	159.2
Radiant heat recovered (MW)	216	216	157	157	157	157
Natural Gas rate (tonne/h)	–	–	38.1	38.1	38.1	38.1
Plant Electricity consumed (MW)	232.2	198.4	198.5	174.0	229.2	196.8
Gasoline produced (ML/yr)	232.0	232.0	281.1	281.1	250.4	250.4
Distillate produced (ML/yr)	627.2	627.2	748.3	748.3	665.5	665.5
Sulfur produced (ktonnes/yr)	99.8	99.8	72.5	72.5	72.1	72.1
Direct GHG emitted (MtonnesCO_2eq/yr)	0.14	3.58	0.16	2.61	0.13	2.85
Indirect GHG emitted (MtonnesCO_2eq/yr)	0.36	0.002	0.58	0.27	0.3	0.19
Total cradle to plant exit gate GHG (kgCO_2eq/GJ)	18.72	135.91	23.32	91.23	15.55	108.17
Total capital Cost (M$)	1116.8	944.8	1140.3	976.6	1129.3	958.2
Annual operating Cost (M$/yr)	246.8	371.4	282.2	363.2	268.4	372.1
NPV ($million)	74.3	−588.7	289.2	−3.7	125.3	−412.7
Min. Diesel Selling Price ($/gal)	1.78	2.32	1.62	1.85	1.74	2.18
Max. Petcoke price ($/tonne)	6.4	−44.1	35.6	−0.4	15	−44.3
CCA ($/tonne$CO_2$eq)	459	–	463	–	308	–

For ease of comparison with current market price, the minimum diesel selling prices for each of the configurations was computed. Even with carbon emission taxes, it can be seen that all the plants with CCS have MDSPs which are competitive with the current refinery diesel wholesale price of $1.85/gal [56]. Those without CCS are not profitable due to the carbon taxes assumed in this analysis, and hence cannot compete. However, with no carbon taxes on emissions, they turn out to be more profitable given the reduced investment and operating costs. At this scale of operation, the CCAs for the PG-ENGR and PG-INGR designs are $308/tonne and $463/tonne respectively, clearly showing the strong effect of economy of scale. Nevertheless, the $308/tonne CCA for the PG-ENGR design is still comparable to or better than some other alternative fuels, such as biological biobutanol ($472/t$CO_2$e) [68], thermochemical biobutanol ($136/t$CO_2$e) [69], biodiesel ($400/tCO_{2e}) [70], or corn ethanol (potentially up to $750/t$CO_2$e) [70].

Another important metric explored was the maximum petcoke price since the valuation of petcoke waste is uncertain. In the previously discussed results, the petcoke price was assumed to be $0/tonne [14] since it is a locally produced waste. However, the maximum petcoke price was computed as the price at which the NPV becomes zero, with all other parameters at their default values. As shown in Table 8, for all the CCS plants, the maximum petcoke prices were between $6/tonne to $36/tonne. For the non-CCS plants, the maximum price was negative, meaning that in order for those plants to be profitable, the processing plant would have to be paid to take waste petcoke off of the hands of the refinery.

3.5. Sensitivity analysis

The economic results presented above are based on investment assumptions and current market prices of commodities which are uncertain and can vary widely due to plethora of reasons such as inflation, demand, politics, etc. Thus, there is a need to carry out a sensitivity analysis. Fig. 7 shows the effect of the petcoke purchase price on NPV. Between $0/tonne to $50/tonne, the PG-INGR configuration with CCS shows to be the best design and profitable as long as the petcoke price is below $45/tonne. The PSG and PG-ENGR CCS design are only profitable when petcoke price is no more than $5/tonne and $15/tonne respectively. As the petcoke price increased, the PG-ENGR faired better because of the reduced proportion of petcoke it consumes when compared to the PSG design. Without CCS, none of the plants are profitable (because of the assumed carbon tax).

The natural gas price is also crucial to the economics of the plant. The range of natural gas prices evaluated is representative of the previous 10 years' price history, and shown in Fig. 8. As our utilities were assumed to be a function of the natural gas price, the gas price has significant effect on all the designs, even those that do not use natural gas as a feedstock. Unlike the PGS design with CCS, the PSG design without CCS (less utility consumed) had an increase in NPV when the gas price was increased due to the extra revenue generated from the HPS produced in the gasifier radiant coolers. Compared to the PG-ENGR design which also produces steam in the radiant cooler, the cost of amount of natural gas feed consumed balanced the extra revenue from selling the steam. Despite this condition, the PG-INGR design which uses its heat for syngas generation is still a good investment at a gas price of $4/MMBtu or below.

The effect of penalizing a plant by the amount of CO_2 emitted was evaluated in Fig. 9 and it shows that plants with CCS are almost independent of emissions tax since they have almost no CO_2 emissions. Without CCS, the impact of the CO_2 penalty is well pronounced as can be seen by the huge drop in NPV. The PSG and PG-ENGR designs remain profitable at a tax rate of about $30/tonne while the PG-INGR could survive till $49/tonne. One observation is that running the PSG without CCS is more profitable than that of PG-ENGR if the CO_2 tax is within $20 given the total emissions (per GJ basis) of the design for a cheaper penalty.

The effects of shareholders interest on the plant is shown in Fig. 10. This analysis showed that the CCS plants would have a positive NPV when operated at the recommended D/E ratio of 50:50 [51]. While the PG-INGR design without CCS is profitable at D/E ratio of 81:19, it is not surprising that the PSG and PG-ENGR designs are not profitable even at a D/E ratio of 100/0. Unlike the D/E ratio which had no much impact on the economics of the CCS designs, the effects of IRR (Fig. 11) on the NPV showed to be significant.

Interest rates higher than 15% give poor economics for the CCS PG and PG-ENGR designs while the PG-INGR is profitable at up to 18%, which compares well to the recommended IRR of 20% by Worhach et al., [51].

With much uncertainty in the price of crude oil, the price of diesel and gasoline are subject to change. Figs. 12 and 13 show the effects of products market price on the profitability of the plant. With only a 4 cents/gal drop in the base price of diesel from our assumed conditions, none of the plants were profitable. Similarly, at a 7 cents/gal drop in gasoline price from the base case was

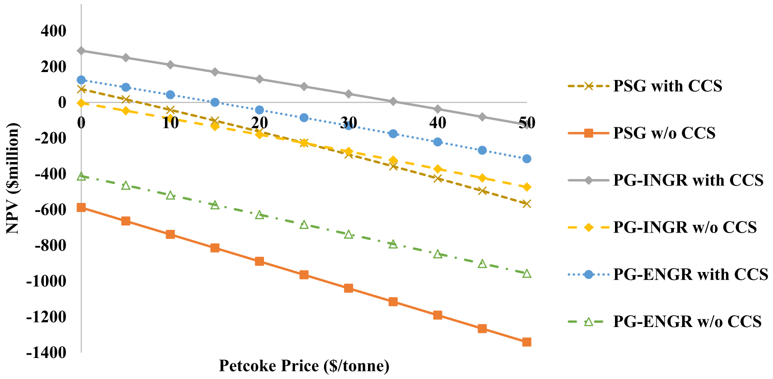

Fig. 7. Effect of petcoke price on NPV.

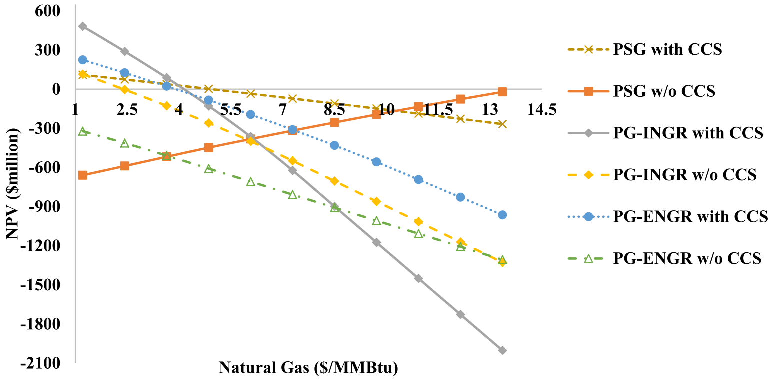

Fig. 8. Effect of natural gas price on NPV.

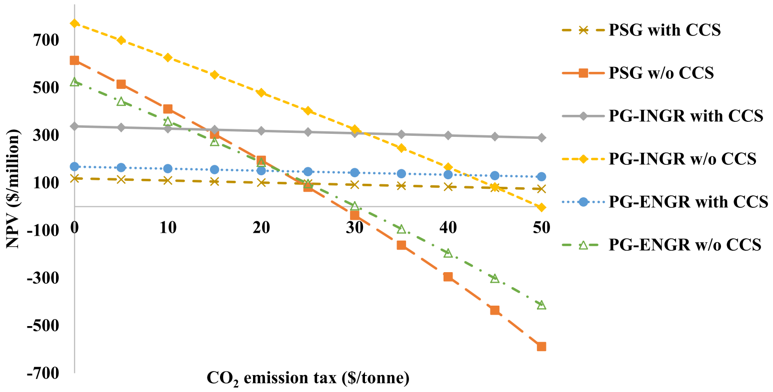

Fig. 9. Effect of CO_2 emission tax on NPV.

enough to bring the NPV below zero of the most profitable process. So, the consideration of this uncertainty would be crucial in future decision making with regards to this process.

To justify the assumption for the cost of the proposed integrated gasifier radiant syngas cooler and natural gas reformer, Fig. 14 shows the effect of this assumed cost on NPV. PG-INGR with CCS, the design is profitable even when proposed design is double the cost of a traditional gasifier. The PG-INGR design without CCS has a positive NPV when its cost was less than about 48% more than the cost of a traditional gasifier. Hence, the assumption of a 50% cost is conservative.

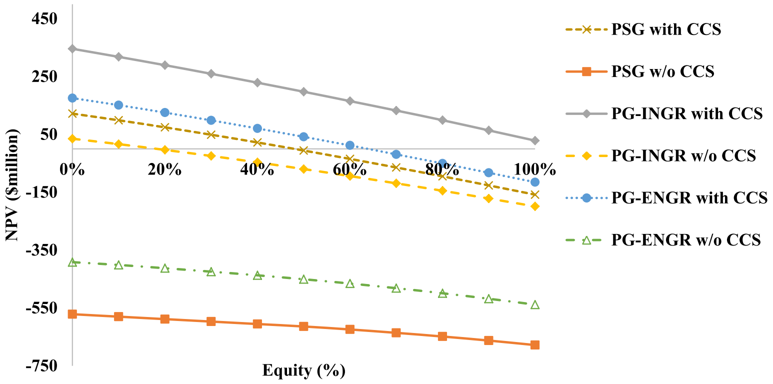

Fig. 10. Effect of Equity price on NPV.

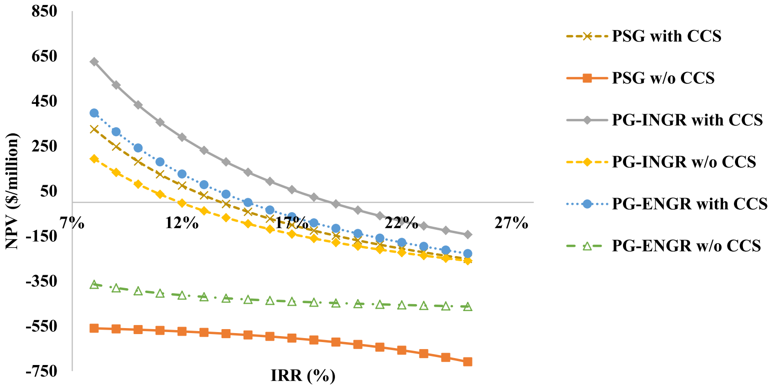

Fig. 11. Effect of IRR price on NPV.

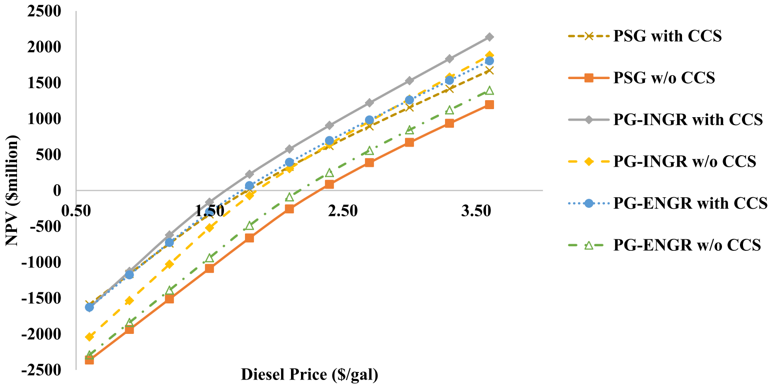

Fig. 12. Effect of diesel price on NPV.

4. Conclusions

The results showed that converting petcoke into liquids with CCS through a traditional gasification route is not profitable nor were the environmental benefits worth the cost. However, by tightly integrating natural gas reforming with petcoke gasification (by performing the gas reforming in the tubes of the radiant syngas cooler), the results were much more promising. This integration strategy uses the excess heat from the gasifier to drive the endothermic reforming process of gas reforming, which has synergistic

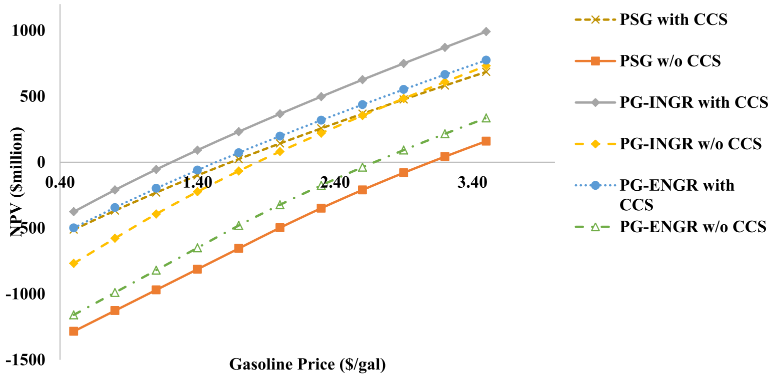

Fig. 13. Effect of gasoline price on NPV.

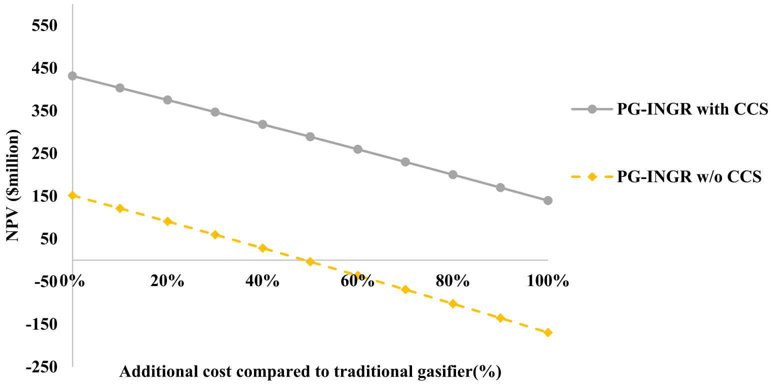

Fig. 14. Effect of PG-INGR gasifier cost on NPV.

benefits. The two syngas streams can be blended together to produce a syngas with an H_2/CO ratio much closer to the ratio needed for FT synthesis. This avoids some of the losses associated with syngas upgrading (such as water gas shift) or high-temperature heat production (for natural gas reforming). The results showed that this resulted in a substantially more efficient process than an equivalent process using the same amount of petcoke and natural gas, but in a more traditional manner.

This translated into a significant economic benefit for the PG-INGR design, and an environmental gain for the PG-ENGR process. Both (with CCS) had a strong business case using the reference market prices. Furthermore, the cradle-to-product GHG emissions were low enough such that there is an incentive to construct the PG-ENGR process for the explicit purpose of GHG emissions reduction. For the standard petcoke consumption rate of 219 t/hr, the cost of CO_2 avoided for PG-ENGR was as low as $193/t$CO_2$e when the process is considered in the context of displacing traditional petroleum fuels. However, the analysis also found that these results are strongly influenced by key parameters such as plant capacity, interest rates, and fuel prices such that even minor changes in some parameters could cause the process to become a poor investment. There is additional room for improvement as well, since the process has not been optimized, nor have the other potential environmental benefits besides GHG emissions reduction been examined. Therefore, the PG-INGR and PG-ENGR concepts are worth further study, but the effects of market uncertainty should be carefully considered.

Acknowledgements

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Appendix B. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.energy.2018.08.058.

Nomenclature

Abbreviations

AEA	Aspen Energy Analyzer
AF	annualization factor
APEA	Aspen Process Economic Analyzer
APC	annual production capacity
ASU	air separation unit
CCA	cost of CO_2 avoided
CCS	carbon capture and storage
CC	composite curves

DW&B	direct wages and benefits
FF	fuel fractions
FT	Fischer-Tropsch
GCC	grand composite curves
GHG	greenhouse gas
HEN	heat exchanger network
HHV	higher heating value
HTWGS	high temperature water gas shift
HPS	high pressure steam
IRR	internal rate of return
LTWGS	low temperature water gas shift
MACRS	modified accelerated cash recovery system
MER	minimizing energy requirement
MDSP	minimum diesel selling price
MILP	mixed integer linear program
MW&B	maintenance, wages and benefits
M&O	maintenance overhead
MDEA	methyl di-ethanolamine
NPV	net present value
PSG	petcoke standalone gasification
PG-INGR	petcoke integrated natural gas gasification
PG-ENGR	petcoke external natural gas gasification
RM	refinery margins
SEP	separator block
SW&B	salaries, wages, and benefits
TAC	total annualized cost
TDEC	total direct equipment costs
TPC	total product cost
WGS	water gas shift
WHB	waste heat boiler
WP	wholesale price

Greek

η	efficiency

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Chapter 3

Analysis of the environmental impacts of petroleum coke to liquids processes.

The content of this section is a **published reprint** of the following peer-reviewed publication,

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Comprehensive environmental impact assessment of a combined petroleum coke and natural gas to Fischer-Tropsch diesel process

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ABSTRACT

In this study, a well-to-wheels life cycle assessment was conducted to determine the environmental impacts from disposing of petroleum coke by converting it into liquid fuel. Specifically, this work is an extension of the life cycle assessment of the petcoke standalone gasification to diesel study which also includes two new pathways for converting petroleum coke and natural gas to Fischer Tropsch diesel operated with and without carbon capture and sequestration (CCS). Impact categories were calculated using the EPA's TRACI 2.1 US-Canada 2008 midpoint method in SimaPro software. In addition, the impact of grid emissions on the overall process was assessed using two representative Canadian locations with high (Alberta) and low (Ontario) grid emissions. The results of each impact category were compared among the designs and against conventional petroleum and oil sands derived diesel. Key findings showed that the proposed designs when operated with CCS in the low-emissions-grid location had life cycle GHG emissions between 281–291 gCO_2-eq/km compared to the conventional petroleum and oil sands derived diesel with GHG emissions of 305 and 348 gCO_2-eq/km respectively. Nevertheless, the various tradeoffs between processes indicated that there was no clearly superior design among the candidates. However, the design which uses a natural gas reformer that is integrated directly into the radiant syngas cooler of a petcoke gasification unit has the lowest cost of CO_2 avoided ($144/$tCO_2$-eq), and so is likely the best choice for reducing environmental impacts.

1. Introduction

Petcoke is the unwanted solid waste that is produced when petroleum residues or oil sand bitumen is upgraded to lighter fractions. Despite the high market value of these liquids, petcoke is generally of limited use. For example, unprocessed petcoke from a coker unit is usually high in sulfur and considered low grade (fuel grade); as such, it is most commonly used as an inexpensive fuel source for boilers, cement kilns, etc. However, government restrictions on petcoke combustion have prohibited its use as fuel, at least in parts of North America (Stockman, 2013). Some petcoke can also be further processed (calcination operation) to produce high-grade (anode grade) petcoke, which is used in the steel and aluminum industries. The remaining produced petcoke (generally unprocessed petcoke) is stockpiled indefinitely, which poses a number of problems. Besides occupying valuable land at storage locations, this stockpiled coke is responsible for a variety of environmental impacts, such as air and water pollution, as well as having potentially detrimental effects on the respiratory health of nearby populations (Andrews and Lattanzio, 2020). These concerns highlight the need for the development of a benign petcoke "end of life" strategy.

Wabash River Energy Ltd.'s 262 MWe power plant offers one potential solution for disposing of low-grade petcoke, as its GE 7FA turbine is driven by syngas generated by petcoke gasification (Amick, 2000). Additionally, Wabash River Energy has also shown that petcoke can be used in a coal gasifier without any operational issues. The Tampa Electric Polk Power Station provides another possible solution for petcoke disposal, as its integrated gasification combined cycle (IGCC) utilizes a combination of petcoke and coal to produce electricity (DOE/NETL, 2004). Besides power generation, petcoke has been used for fuel and chemical production. For instance, the Coffeyville syngas plant uses petcoke from the Coffeyville refinery as a zero-value waste fuel to produce 1300 tons of ammonia per day (Brown, 2013). This clearly illustrates how petcoke stockpiles can be used to produce value-added products. Similarly, polygeneration studies conducted by the US Department of Energy's National Energy Technology Laboratory (NETL) have found that the conversion of petcoke to hydrogen, fuel gas, industrial-grade steam, and Fischer-Tropsch (FT) liquid fuels is an economically attractive option when petcoke is zero cost (Kramer, 2003). A different study examined the optimization of petcoke-natural gas

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Nomenclature

AP	Acidification potential
CAPEX	Capital expenditure
CCA	Cost of CO_2 avoided
CCS	Carbon capture and storage
CP	Carcinogenic potential
D/E	Debit-to-equity ratio
EP	Eutrophication potential
ETP	Ecotoxicity potential
FFD	Fossil fuel depletion
FT	Fischer-Tropsch
GHG	Greenhouse gas
GWP	Global warming potential
HEN	Heat exchanger network
IRR	Internal rate of return
LCA	Life cycle assessment
MDSP	Minimum diesel selling price
MDEA	Methyl di-ethanolamine
NCP	Non-carcinogenic potential
ODP	Ozone depletion potential
OPEX	Operating expenditure
PDD	Petcoke derived diesel
PSG	Petcoke standalone gasification
PG-INGR	Petcoke integrated natural gas gasification
PG-ENGR	Petcoke external natural gas gasification
RE	Respiratory effects
SF	Smog formation

polygeneration for the production of olefins, methanol, dimethyl ether (DME), and FT liquids (Salkuyeh and Adams, 2015). The results of this study showed that petcoke-natural gas polygeneration is not economical when petcoke is used above a certain ratio (petcoke/natural gas). Petcoke has also been proposed for use in power-to-gas technology in order to produce a range of products, including fuels and chemicals (Ranisau et al., 2017). That study was the first to employ a mixed-inter linear programming to assess the economics of using electrolysis and surplus grid electricity for petcoke disposal in a polygeneration system. Recently, we presented six strategies for converting petcoke to FT diesel and gasoline that focused on design efficiency, NPV, and GHG emissions (Okeke and Adams, 2018). Our results indicated that this approach is economically promising when petcoke gasification is tightly integrated with a natural gas reforming process. Although the conversion of petcoke to liquids has tremendous technical and economic potentials, detailed studies of this process' environmental impacts do not exist. Therefore, a life cycle assessment—which is a systematic approach to evaluating the environmental impacts of a particular process to ascertain its overall effects on the eco-system—was conducted in this work.

Alternatives liquid fuels, such as those made from coal, gas, and biomass, can potentially have lower life cycle impacts and/or be competitive with conventional fuels in terms of actual cost or cost of CO_2 avoided (Hoseinzade and Adams, 2019; Okeke et al., 2019). In many cases, though, alternative fuels have none of these advantages. For example, Jaramillo et al. (2009) conducted a life cycle assessment that compared GHG emissions from vehicles (fuel economy of 19.1 km per liter) operated with coal-to-liquid (CTL) fuels against coal-based electricity powered plug-in hybrid electric vehicles (PHEV) and coal-based hydrogen-fuel-cell vehicles (FCV) using a functional unit of gCO_2-eq per km traveled. Their results showed that PHEVs produced less GHG emissions than the CTL vehicle and FCVs, and that the CTL vehicle and FCVs also produced more GHG emissions than petroleum-powered vehicles. Similarly, the NETL conducted a cradle-to-grave (CTG) life cycle assessment comparing the relative GHG emissions of FT diesel (FTD) made from Illinois #6 coal and petroleum-based diesel for sport utility vehicles (SUV) (Marano and Ciferno, 2001). Their results showed that the coal-derived diesel had a GHG life cycle of 583.5 gCO_2-eq/km,

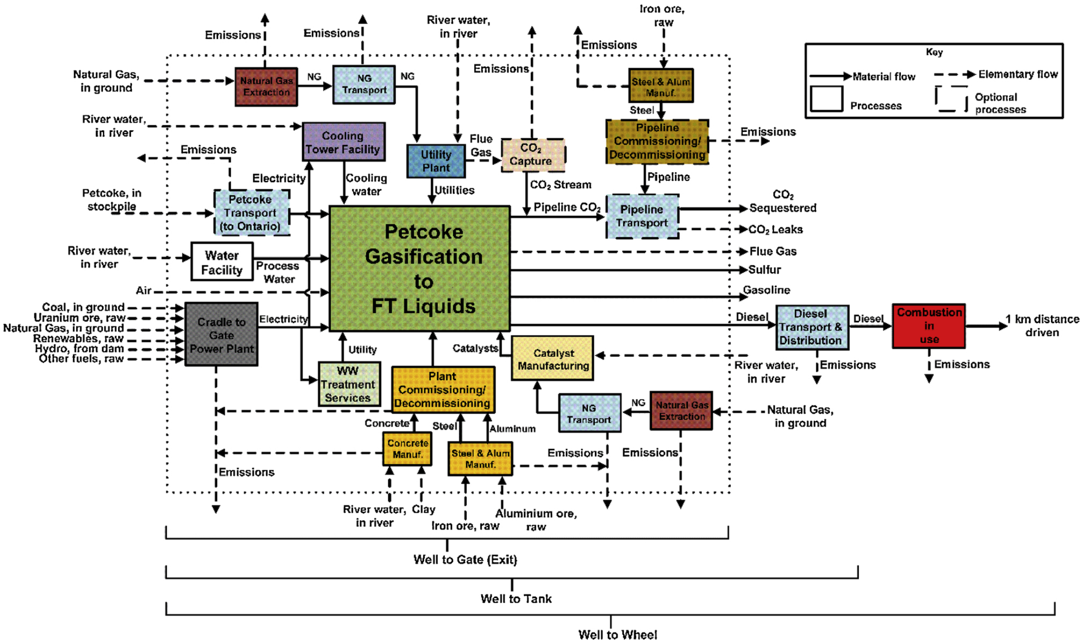

Fig. 1. System boundary of the petcoke standalone gasification design.

while the Wyoming sweet crude oil had a GHG life cycle of 290.8 gCO_2-eq/km. For the gas-to-liquid (GTL) process, Forman et al. (2011) used a substitution allocation method to perform a well-to-wheels (WTW) GHG life cycle assessment with the results of their assessment showing a GHG emissions of 292.9 gCO_2-eq/km using a vehicle fuel economy of 8.6 litres per 100 km. Biomass-to-liquid (BTL) fuel production has also received considerable research attention due to its so-called “carbon neutrality” and reduced environmental impact. For example, Kreutz et al. (2008) performed a BTL LCA and found that, when the gasifier char carbon is assumed to be sequestered, BTL has a negative GHG emissions life cycle, even without CO_2 capture and sequestration.

Although these examples demonstrate that other alternative fuel pathways are promising from an environmental standpoint, studies that address the environmental aspects of petcoke-to-liquids are limited. Recently, we presented the WTW LCA of petcoke standalone gasification (PSG) which showed to have a reduced GHG emission compared to conventional and oil sands diesel (Okeke and Adams, 2019). In this work, we have extended the LCA of the PSG system by recomputing the GHG emissions using the 5th IPCC assessment report factors and also estimated the cost of CO_2 avoided. In addition, two new designs that combines petcoke and natural gas to FT diesel were also presented in order to ascertain the environmental benefits of such synergy. The new design configurations studied are petcoke gasification and external natural gas reforming (PG-ENGR) and petcoke gasification integrated with natural gas steam reforming (PG-INGR) both with and without CCS. Our prior work (Okeke and Adams, 2018) on these configurations consisted of techno-economic analyses that used Aspen Plus v10 process-simulation software to compute process stream flows, energy consumption and production, equipment sizes and costs, and profitability. Therefore, this study aims to examine the environmental impacts of a petcoke-to-liquids process known as the petcoke-derived-diesel (PDD) process. Altogether, the environmental performance of six configurations were presented and compared amongst each other and against the conventional and oil sands diesel.

2. Life cycle process methodology and assumptions

2.1. Goal, scope, and boundaries

The goal of this study was to assess, quantify, and compare the environmental effects of six PDD process configurations—PSG, PG-ENGR, and PG-INGR—both with and without CSS.

The scope of this analysis comprised the WTW material and energy inputs and outputs, along with their emissions over the entire life cycle of each PDD process. The system boundaries considered for each configuration will include the well-to-plant exit gate (WTG), PDD transportation and distribution (WTT), and the subsequent use of PDD in a compression-ignition direct-inject (CIDI) vehicle (WTW), thus indicating the petcoke’s “end of life.” Figs. 1–3 depict this process for each of the analyzed configurations. For reference, the proposed designs were compared to conventional petroleum and oil sands derived diesel obtained from the GREET model (GREET Model, 2017) with input data and emissions given in the supplementary document. To this end, an energy allocation method was used to determine emissions allocation for the gasoline and diesel produced in our proposed designs. In order to further facilitate comparison, the inventories of the petcoke, conventional petroleum, and oil sands diesel processes were normalized to 1 km distance driven in a standard passenger car.

2.2. Impact assessment calculation

The life cycle impact assessment (LCIA) categories were calculated using the Tool for Reduction and Assessment of Chemicals and other environmental Impacts (TRACI 2.1) v1.04 midpoint method in the life cycle flow-sheeting software, SimaPro v 9.0. The TRACI method is a US Environmental Protection Agency (EPA) LCA methodology that provides the characterization factors used for LCIA and quantifies the impacts of the process inputs and their corresponding emissions on a specific impact category in an equivalent unit (EPA, 2018). Table 1

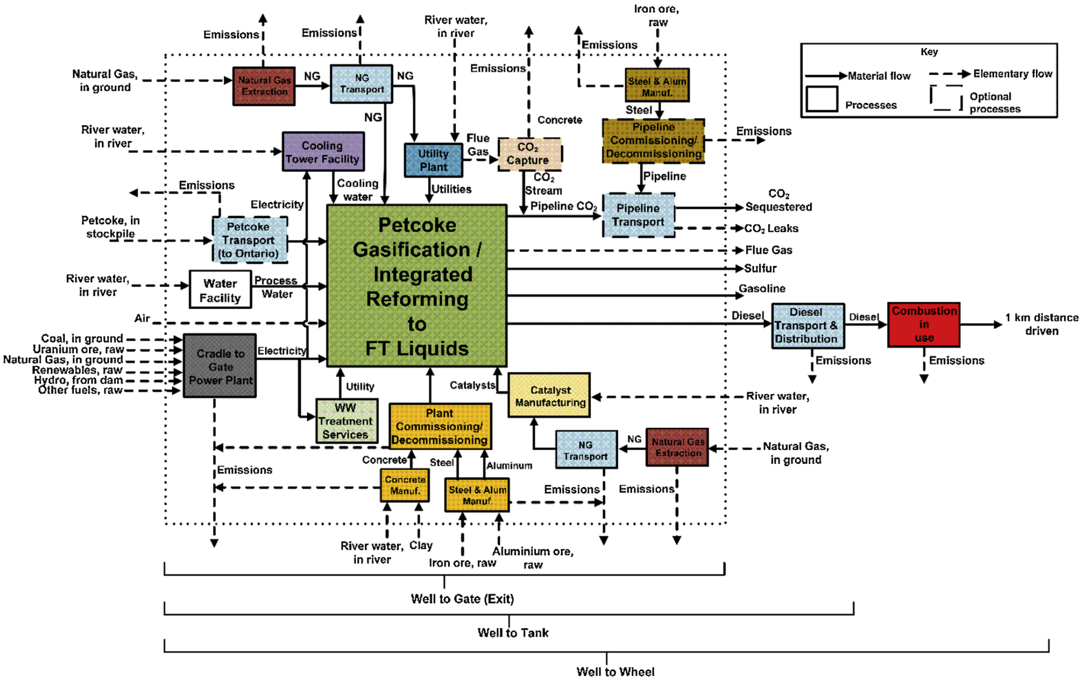

Fig. 2. System boundary of the petcoke gasification integrated with natural gas reforming.

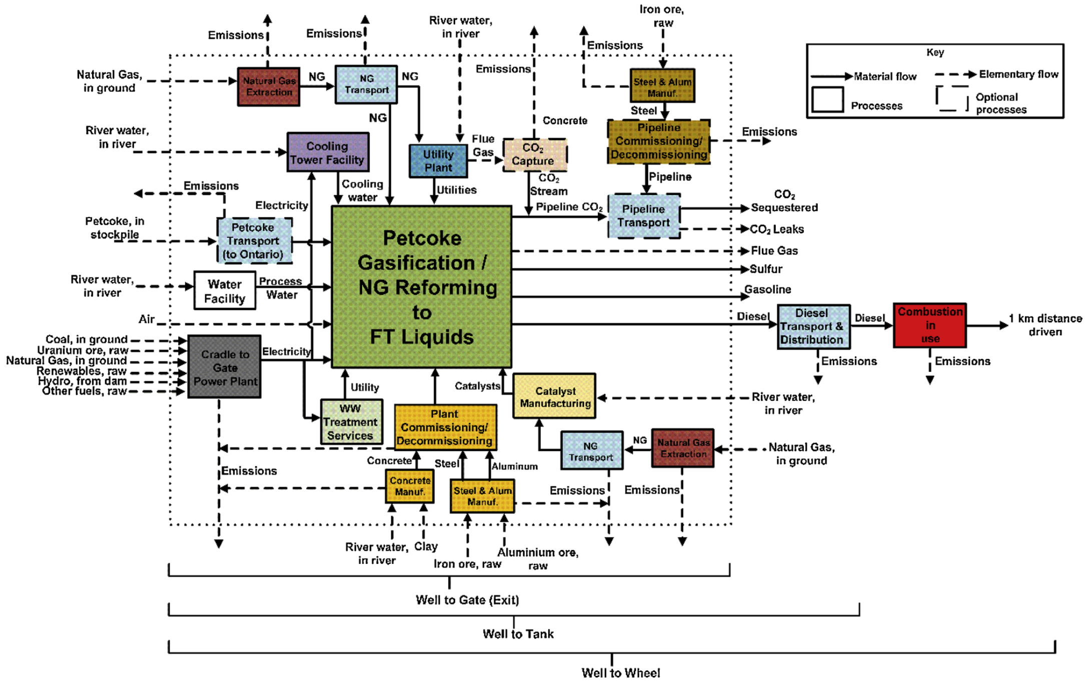

Fig. 3. System boundary of the petcoke gasification and external natural gas reforming.

Table 1
Midpoint impact categories considered in this study.

Impact category	Abbreviation	Units	Level of impact
Ozone depletion potential	ODP	kg CFC-11-eq	Global
Global warming potential	GWP	kg CO_2-eq	Global
Smog formation	SF	kg O_3-eq	Regional
Acidification potential	AP	kg SO_2-eq	Regional or National
Eutrophication potential	EP	kg N-eq	Regional or National
Carcinogenics potential	CP	CTUh	National
Non-carcinogenic potential	NCP	CTUh	National
Respiratory effects	RE	kg PM2.5-eq	Regional or National
Ecotoxicity potential	ETP	CTUe	National
Fossil fuel depletion	FFD	MJ surplus	Global

shows the midpoint impact categories that were considered in this study, along with their corresponding extent or area of impact. Unlike our previous work (Okeke and Adams, 2019), the global warming potential (GWP) computed in this study followed the Intergovernmental Panel on Climate Change's (IPCC) 100-year metric characterization factor updates for methane (CH_4) and dinitrogen monoxide (N_2O), which were 30 and 265, respectively (IPCC, 2015). Thus, we recomputed the impact assessments of the PSG design presented in our prior work (Okeke and Adams, 2019) using these updated factors.

2.3. Assumptions

The characteristics of the consumables used in this study are shown in Table 2.

In addition, the following assumptions were made:

- The petcoke used in this study is delayed coke produced as an unintentional and undesired waste product from oil sands upgrading by Suncor Energy Inc. in Athabasca, Alberta. Since the petcoke is classified as waste, there are no indirect emissions associated with its production, as all emissions associated with refinery upgrading are instead associated with the saleable refinery products (Keesom et al., 2009). Therefore, all emissions attributed to petcoke in this study are direct emissions from the considered PDD processes and indirect emissions not associated with petcoke (such as natural gas procurement); the emissions calculation for each process begins at the petcoke stockpile, and includes transportation and handling for conversion purposes, as well as direct process emissions.
- The petcoke and/or natural gas conversion facility locations used in this work were considered to be constructed in a "brown field." One facility was within close proximity to the petcoke stockpile in Athabasca, Alberta, while the other was located near existing refineries in Sarnia, Ontario. Hence, changes in direct and indirect land use were not considered in this analysis, as there was no additional land occupation associated with the brown field

Table 2
Assumed composition of consumable materials.

Delayed coke (Watkinson et al., 1989)			
HHV (MJ/kg)	34.7		
Ultimate analysis (wt. % dry)			
C	84.9	Cl	0
H	3.9	Ash	3.1
N	1.3	O (diff)	0.8
S	6		
Proximate analysis (wt. %)			
Moisture	1.8	Fixed carbon	83.3
Volatile matter	11.9	Ash	3
Natural gas (Klara et al., 2007)			
HHV (MJ/kg)	52.97		
Components (%mole)			
CH_4	93.9	CO_2	1.0
C_2H_6	3.2	C_4H_{10}	0.4
N_2	0.8	C_3H_8	0.7

assumption. However, transportation-related emissions differed depending on the location scenario.

- Emissions from gasifier slag disposal were not considered because this material can also be used as concrete for road construction (Slag Cement Association, 2018).
- The fugitive emissions of captured CO_2 during pipeline transportation were assumed to be 1% of the transported CO_2 on a mass basis (Draucker et al., 2010).
- The vehicle fuel economy and combustion emissions used in this study were based on the GREET model (GREET Model, 2017).

3. Process description

3.1. Petcoke standalone gasification design (PSG)

Instead of stockpiling, petcoke is ground and mixed with water at ratio of 44 wt%:56 wt% (H_2O: petcoke) to form a slurry. Syngas is then produced by feeding the slurry into the petcoke E-gas gasifier, which uses 99.5 % pure oxygen delivered from an air separation unit located within the analysis boundaries. The overall gasification reaction—namely, pyrolysis, volatile combustion, char gasification, and sulfur reaction—was considered when modeling the process (Okeke and Adams, 2018). The petcoke E-gas gasifier was designed to operate at 1426 °C and 56 bar. Due to the gasifier's high operating temperature, boiler feed water (BFW) is usually used to provide the cooling duty required by the hot syngas in a radiant syngas cooler (RSC), which in turn produces high-pressure steam (HPS) (Zhu, 2015). The use of BFW as a syngas coolant distinguishes this design configuration and that of PG-ENGR from the PG-INGR configuration. The model assumed carbon conversion in the gasifier to be 99 % (Amick, 2000), with unconverted carbon and trace metals such as nickel and vanadium exiting the gasifier as slag (Basu, 2006). The syngas is cleaned, reformed to raise the H_2:CO ratio, and sent to the acid-gas removal unit to remove H_2S (which is converted to sulfur via Claus process) and capture CO_2 (which is compressed and sequestered) before being catalytically reformed to produce FT fuels. While 90 % of the unconverted syngas was recycled, the remaining portion was used for steam generation (boiler flue gas flared to the environment). This description summarizes the subprocess, known as "Petcoke Gasification to FT Liquids," illustrated in Fig. 1. The mass and energy flows (life cycle inventories) were taken directly from Okeke et al.[1] (Okeke and Adams, 2018) which can be found in the supplementary documents. In addition to the flue gas, fugitive emissions (especially CO_2 emissions) in wastewater treatment were also considered. Fig. 1 also provides a detailed account of all indirect material and energy inputs into the PPD plant, along with their associated emissions.

3.2. Petcoke gasification integrated with natural gas reforming (PG-INGR)

This design configuration combines the use of petcoke and natural gas as feed for the production of FT diesel. As with the PSG configuration, this process utilizes petcoke gasification; however, unlike the PSG configuration, the PG-INGR configuration uses natural gas to cool the hot gasifier syngas. In this design, pre-reformed natural gas and steam are sent through the gasifier RSC tubes packed with steam methane reforming (SMR) catalysts. The hot petcoke-derived syngas drives the endothermic steam-reforming process, which also cools the syngas (Okeke and Adams, 2018). The syngas produced by this design is a blend of the petcoke gasifier syngas and the reformed natural gas derived syngas, and it is used for liquid fuel production, much like the syngas produced by the PSG design. This description summarizes the subprocess, known as "Petcoke Gasification Integrated Reforming to FT Liquids," shown within the system boundary of Fig. 2.

3.3. Petcoke gasification and external natural gas reforming (PG-ENGR)

Although similar to both the PSG and PG-INGR designs, the PG-ENGR design is distinct in its configuration. As with the PSG configuration, the PG-ENGR configuration utilizes BFW to cool the syngas produced by hot petcoke gasification in an RSC. In addition, the PG-ENGR configuration also combines petcoke gasification and natural gas reforming to produce liquid fuels. This subprocess, known as "Petcoke Gasification / NG Reforming to FT Liquids," is depicted in Fig. 3. However, unlike PG-INGR, the PG-ENGR configuration uses a standalone auto-thermal reformer to convert natural gas to syngas with a high H_2:CO ratio. The rationale for the PG-ENGR design is to effectively compare its performance with that of PG-INGR configuration since both designs also use natural gas as feedstock, unlike the PSG design which uses only petcoke. The system boundary for the PG-ENGR design is shown in Fig. 3.

3.4. Other sub-processes

3.4.1. Plant construction

The materials used to construct the plant and energy inputs and emissions for the PDD system were both considered in this study. Given the similarities between the PDD and CTL processes, the material, energy inputs, and the emissions associated with the construction and decommissioning of the PDD process (all scenarios) were all estimated using data from an NETL study of a CTL plant (NETL, 2010).

3.4.2. Petcoke transport

Due to the vast differences in electricity grid carbon intensity across possible plant locations, we considered a scenario that involves the transportation of petcoke from Athbasca, Alberta to Suncor Energy Inc.'s yard, which is located in Sarnia, Ontario. This approach was selected because it was expected to be helpful in evaluating the extent to which electricity grid emissions impact the PDD process. The Ontario location was chosen because it was considered to be representative of a site with low electricity grid emissions. Plants are typically designed to enable coke to be deposited from the cokers into the open hoppers of the rail cars with maximum ease (Andrews and Lattanzio, 2020). As such, the emissions associated with loading petcoke onto a train are negligible and were not considered. In addition, it is assumed that the train being used is a diesel-powered commercial cargo train that travels on existing trans-Canada routes for a distance of 3114 km, and the direct emissions of transport are considered. It is also assumed that petcoke transportation represents only a fraction of the train's cargo over its lifetime. Thus, the material, energy inputs, and emissions associated with the construction of the trains were considered negligible compared to the direct diesel emissions associated with trans-Canada transport.

3.4.3. Electricity consumption

Since electricity generation and emissions vary widely from grid to grid, each local grid's impact on the entire life cycle of the PDD process was considered. In Canada, for example, the provinces of Alberta and Ontario have a huge disparity in emissions due to the different energy sources making up the electricity grid in 2017 (Table 3). While Ontario has low carbon emissions due to its high dependency on nuclear and hydroelectric energy, Alberta is largely dependent on coal, which is inherently carbon intense. Thus, Alberta and Ontario suitably act as representative examples of electricity grids with high and low emissions. The cradle-to-grid emissions of the Ontario and Alberta electricity grids used in this analysis are shown in Table 3. These were calculated by combining the indirect emissions associated with extracting fuel sources and transporting them to electricity generation facilities (Mallia and Lewis, 2013) with the as-reported 2017 direct power generation emissions by Environment and Climate Change Canada (2020), using

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[1] The Aspen Plus flowsheet can be accessed from http://psecommunity.org/LAPSE:2018.0148

Table 3
Alberta and Ontario electricity grid: sources and emissions used in this study.

Source	Ontario			Alberta		
	% Gen. Contr.	Indirect[a] emissions (gCO_2-eq/kWh)	Power Plant Construction & Direct Operation[b] emissions (gCO_2-eq/kWh)	% Gen. Contr.	Indirect[a] emissions (gCO_2-eq/kWh)	Power Plant Construction & Direct Operation[b] emissions (gCO_2-eq/kWh)
Nuclear[c]	61	1.94	1.72	–	–	–
Coal[d]	–	–	–	60	82.16	626.24
Natural gas[e]	4	2.96	16.20	28	20.82	131.00
Hydro[f]	27	0	4.01	3	0	0.5
Other fuels[g]	1	–	0.95	1	–	0.03
Other renewables[h]	7	1.22	0.53	7	1.20	0.52
Total Elec. Gen. emissions (gCO_2-eq/kWh)			**29.5**			**862**

[a] Consist of emissions for fuel extraction, processing, and transportation to generation facility.

[b] Includes as reported generation emissions (Environment and Climate Change Canada, 2020) and construction/decommissioning emissions (Mallia and Lewis, 2013).

[c] Estimated based on a uranium efficiency of 60 %.

[d] Estimated based on coal fired power plant of 30 % efficiency.

[e] Calculated based on natural gas picking power facility of 35 % efficiency.

[f] Estimated based on a hydro electricity facility of 95 % efficiency.

[g] As reported data due to limited information.

[h] Calculated based on a wind farm with an average efficiency of 18 %.

some assumptions for average plant efficiency as noted in Table 3. These numbers are for AC, grid quality, high voltage electricity leaving the power plants and entering the grid, and does not include transportation or voltage stepdown, which is not considered in this work.

3.4.4. Cooling tower system

To determine the minimum energy requirements of the entire system, we used the heat exchanger network (HEN) design described in our previous work on petcoke-to-liquid fuels processes (Okeke and Adams, 2018). A mechanical evaporative cooling tower system was modeled to satisfy the plant's cooling demands, with water being supplied from a nearby river. The electrical demands of the tower's pump and fan were estimated using Turton et al's. (2008) correlations, assuming that an average wet bulb temperature of 11 °C would be sufficient to maintain cooling.

3.4.5. Utility & CO_2 capture

The heating duty requirements of each PDD process were also estimated based on the heat exchanger network (HEN) design. The required utilities included low-pressure steam (LPS), medium-pressure steam (MPS), high-pressure steam (HPS), and fired heat (FH). To satisfy the different steam-pressure levels and fired-heat demands, natural gas combustion was modeled in the prior work (Okeke and Adams, 2019) in Aspen Plus and fed to the steam boilers and furnace to generate steam and FH, respectively. The steam boilers and furnace had efficiencies of 95 % and 90 %, respectively (NETL, 2010). For the PDD plant scenario with CCS, ProMax® was used in the prior work (Okeke and Adams, 2019) to model the boiler and furnace flue gas capture so that 90 % of the CO_2 would be captured by methyl diethanolamine (MDEA) promoted with Piperazine. Table 4 shows the utility plant direct emissions data used in this study. The associated flue gas emissions are the direct emissions from natural gas combustion used to provide the heat to generate the corresponding utility, expressed in emissions per GJ of utility delivered. The CCS cases consider 90 % CO_2 capture from this combusted natural gas, and also consider the additional parasitic electricity consumption accordingly in balance of plant considerations.

As shown in Figs. 1–3, CCS-enabled designs compress the captured CO_2 to a supercritical condition (153 bar) and transport it to the sequestration site via the CO_2 pipeline, while the flue gas is released into the environment. When the plant is operated without CCS, all combusted CO_2 products are vented into the atmosphere.

3.4.6. CO_2 transport pipeline construction

Since CO_2 capture is not an integral part of liquid fuel plants, each PDD process considered the material, energy inputs, and emissions associated with the construction and decommissioning of a CO_2 transportation pipeline were estimated based on a prior NETL study (NETL, 2012) for a 160 km distance and expressed on the basis of kg of CO_2 transported. Fugitive emissions of CO_2 during transportation were also considered and included in this analysis. For the Ontario plant, captured CO_2 can either be stored in existing oil and gas reservoirs or the saline aquifers in southern Ontario near Lake Erie (Shafeen et al., 2004; Carter et al., 2007) which is approximately 200 km from the Suncor facility, while the Alberta location can use the Quest carbon capture and storage facility (NRC, 2020) with an estimated distance of 151 km.

3.4.7. Wastewater treatment

The wastewater treatment (WWT) facility was not directly modeled in this study. However, the emissions generated as a result of treating the produced wastewater were considered to be a burden of the PDD plant. Thus, a WWT-facility-specific emission of 1.05 kW h/m^3 (Singh et al., 2012) was used, with the estimated environmental impacts being based on local grid emissions.

3.4.8. Catalyst manufacturing

The GREET model was used to obtain the material used to manufacture the catalyst, as well as the associated energy consumption and emissions data (GREET Model, 2017). However, the emissions associated with transporting the catalyst from the manufacturing site to the PDD plant entry gate were not accounted for due to limited data. We assume that these emissions are insignificant given the amount of catalyst consumed in the overall life cycle of the process compared to the amount of product.

Table 4
Plant utility conditions and direct emissions for CCS and non − CCS scenarios.

Parameters	Units	LPS	MPS	HPS	Fired heat
Temperature	°C	204	300	480	1000
Pressure	bar	4	12	50	
Associated flue gas emissions with CCS	$kgCO_2$-eq/GJ	6.49	6.77	7.53	11.63
Associated flue gas emissions w/o CCS	$kgCO_2$-eq/GJ	64.99	67.78	75.26	116.32

3.4.9. Product transportation and distribution

The emissions for the transportation and distribution (T&D) of the PDD to refueling stations were accounted for using GREET model data (GREET Model, 2017). It was assumed that the diesel fuel would be transported via barge, pipeline, and rail, which account for 48.5 %, 46.4 %, and 5.1 % of fuel transportation, respectively. Trucks were assumed to be used solely for local distribution.

3.4.10. Diesel use

Petcoke's end of life is assessed by evaluating the emissions for driving 1 km in a CIDI vehicle with a fuel economy of 8.6 litres per 100 km. For the purpose of comparison, we also estimated the emissions to travel 1 km in a CIDI vehicle of the same fuel economy powered by conventional petroleum and oil sands derived diesel respectively.

4. Results and discussion

4.1. PDD plants: Alberta location

4.1.1. Life cycle inventories and midpoint impacts

The results of the WTW inventory at the Alberta location for each of the six PDD designs with and without CCS are shown in Table 5. For the PSG design (with or without CCS), the consumption rate is 300 g of petcoke per 3.3 MJ_{HHV} of PDD driven (distance of 1 km) and 0.37 MJ_{HHV} of gasoline produced. This corresponds to a petcoke to fuel conversion efficiency of 43.4 % based on higher heating value (HHV), which is defined as the ratio of fuels produced to petcoke processed (Okeke and Adams, 2018). For the Alberta location, the PSG design's life cycle CO_2 emissions with CCS were 467 g/km distance driven, which is equivalent to 1.56 g of CO_2 emitted per gram of petcoke consumed. Without CCS, the PSG design's life cycle CO_2 emissions increased by 83.8 %, which corresponds to 2.86 g per gram of petcoke. To achieve the same thermal input as the PSG design (300 g petcoke per km driven), the PG-INGR design must convert 183 g of petcoke and 81.6 g of natural gas per km distance driven (Okeke and Adams, 2018). As a result, this design's life cycle CO_2 emissions were 419 g/km distance driven with CCS technology, which is 47.8 g of CO_2 per km distance driven emission lower than the PSG design. When PG-INGR was used without CCS, its life cycle CO_2 per gram of petcoke converted was 3.74 g. Conversely, the PG-ENGR configuration had lower emissions than the PSG design but higher than the PG-INGR configuration. This design had life cycle CO_2 emissions that were 9% and 9.6 % higher than those recorded for the PG-INGR configuration with and without CCS, respectively.

Other significant emissions included carbon monoxide, methane, nitrogen oxides, sulfur oxides, and the volatile organic carbon (VOC), which consist of RE, AP, GWP, EP, and SF gases. As expected, the use of CCS increased the emissions of $non-CO_2$ gases due to the parasitic load of the technology. Thus, the trade-off between reducing GHG emissions by capturing CO_2 and emitting other gases which are responsible for other environmental impacts were explored in this study.

Table 6 provides a comparison of the midpoint impact categories of the six PDD designs and conventional and oil sands derived diesel. It could be observed that the ODP of PG-INGR design with CCS was 20.9 % and 17.4 % lower than the PSG and PG-ENGR designs respectively. When compared to the conventional diesel and oil sands diesel, the ODP of all the PDD designs were at least 35.7 % higher and 71.1 % lower respectively. Fig. 4 shows that the ODP of the PDD processes mainly emanated from electricity grid (70 %) and plant construction (21 %). Without CCS, there was a 9–17 % reduction in ODP, which is due to the extra energy required to operate the CCS technology. When CCS was employed, the PSG, PG-INGR, and PG-ENGR designs showed GWPs of 469, 423, and 463 g of CO_2-eq/km distance driven, respectively, with diesel use and electricity grid emissions accounting for at

Table 5

WTW inventory data for the PDD process designs with and without CCS in the Alberta location. Note that "distance driven" is for a diesel-powered vehicle. Gasoline is as an additional side product.

Inventory	PSG	PSG-CCS	PG-INGR	PG-INGR-CCS	PG-ENGR	PG-ENGR-CCS
Input flows (kg unless otherwise specified)						
Petcoke	0.300	0.300	0.183	0.183	0.206	0.206
Natural gas, in ground	0.053	0.065	0.071	0.082	0.092	0.101
Coal, raw	0.062	0.078	0.047	0.055	0.060	0.072
Hydro (MJ)	0.010	0.013	7.7×10^{-3}	9.0×10^{-3}	0.010	0.012
Other renewables (MJ)	0.113	0.143	0.087	0.102	0.111	0.133
Other fuels (MJ)	2.66×10^{-3}	3.37×10^{-3}	2.05×10^{-3}	2.40×10^{-3}	2.60×10^{-3}	3.12×10^{-3}
River water, in river	2.54	2.83	0.65	0.95	1.33	1.44
Iron ore, raw	2.46×10^{-6}	6.80×10^{-5}	2.46×10^{-6}	6.80×10^{-5}	2.46×10^{-6}	6.80×10^{-5}
Aluminium ore, raw	1.51×10^{-6}	1.51×10^{-6}	1.51×10^{-6}	1.51×10^{-6}	1.51×10^{-6}	1.51×10^{-6}
Output flows						
Products flow						
Distance driven (km)	1	1	1	1	1	1
Gasoline (MJ_{HHV})	1.224	1.224	1.224	1.224	1.224	1.224
Sulfur (kg)	0.017	0.017	0.010	0.010	0.012	0.012
Sequestered CO_2 (kg)	0	0.584	0	0.353	0	0.439
Emissions flow to air (kg)						
Ammonia	1.54×10^{-8}	2.12×10^{-8}	1.58×10^{-8}	1.82×10^{-8}	1.87×10^{-8}	2.17×10^{-8}
Carbon dioxide	8.59×10^{-1}	4.67×10^{-1}	6.85×10^{-1}	4.19×10^{-1}	7.47×10^{-1}	4.60×10^{-1}
Carbon monoxide	2.47×10^{-3}	2.48×10^{-3}	2.48×10^{-3}	2.48×10^{-3}	2.48×10^{-3}	2.48×10^{-3}
Dintrogen monoxide	6.75×10^{-7}	6.80×10^{-7}	6.57×10^{-7}	6.60×10^{-7}	6.70×10^{-7}	6.73×10^{-7}
Methane	4.92×10^{-5}	5.38×10^{-5}	9.87×10^{-5}	1.01×10^{-4}	9.14×10^{-5}	9.33×10^{-5}
Nitrogen dioxide	1.80×10^{-7}	1.84×10^{-7}	1.93×10^{-7}	1.95×10^{-7}	1.80×10^{-7}	1.83×10^{-7}
Nitrogen oxides	1.54×10^{-4}	1.63×10^{-4}	1.61×10^{-4}	1.64×10^{-4}	1.62×10^{-4}	1.66×10^{-4}
NMVOC, Non-methane volatile organic compounds	1.39×10^{-6}	1.89×10^{-6}	1.43×10^{-6}	1.64×10^{-6}	1.68×10^{-6}	1.94×10^{-6}
Particulates, $>$ 2.50 µm, and $<$ 10 µm	2.37×10^{-7}	5.31×10^{-7}	4.55×10^{-7}	574×10^{-7}	5.51×10^{-7}	6.57×10^{-7}
Sulfur dioxides	2.84×10^{-6}	1.15×10^{-5}	2.67×10^{-5}	3.06×10^{-5}	2.23×10^{-5}	2.61×10^{-5}
Sulfur oxides	4.12×10^{-4}	8.22×10^{-4}	2.86×10^{-4}	4.46×10^{-4}	5.12×10^{-4}	6.17×10^{-4}
VOC, volatile organic compounds	1.15×10^{-4}	1.29×10^{-4}	1.12×10^{-4}	1.17×10^{-4}	1.19×10^{-4}	1.23×10^{-4}

Table 6
WTW LCA results for the petcoke to diesel plant located in Athabasca, Alberta, for a basis of 1 km distance driven.

Impact categories	Units	PSG	PSG-CCS	PG-INGR	PG-INGR-CCS	PG-ENGR	PG-ENGR-CCS	Conv. Diesel	Oil Sand Diesel
Ozone depletion	kg CFC-11-eq	2.93×10^{-12}	3.52×10^{-12}	2.53×10^{-12}	2.78×10^{-12}	2.92×10^{-12}	3.37×10^{-12}	1.79×10^{-12}	1.22×10^{-11}
Global warming	kg CO_2-eq	8.60×10^{-1}	4.69×10^{-1}	6.88×10^{-1}	4.23×10^{-1}	7.50×10^{-1}	4.63×10^{-1}	3.05×10^{-1}	3.48×10^{-1}
Smog	kg O_3-eq	4.39×10^{-3}	4.64×10^{-3}	4.54×10^{-3}	4.64×10^{-3}	4.61×10^{-3}	4.70×10^{-3}	7.02×10^{-3}	1.20×10^{-2}
Acidification	kg SO_2-eq	5.12×10^{-4}	9.36×10^{-4}	4.29×10^{-4}	5.94×10^{-4}	6.53×10^{-4}	7.62×10^{-4}	3.33×10^{-4}	7.59×10^{-4}
Europhication	kg N-eq	7.59×10^{-6}	9.02×10^{-6}	1.26×10^{-5}	1.33×10^{-5}	1.20×10^{-5}	1.25×10^{-5}	2.01×10^{-5}	3.60×10^{-5}
Carcinogenics	CTUh	1.51×10^{-10}	2.54×10^{-10}	5.71×10^{-10}	6.20×10^{-10}	5.15×10^{-10}	5.51×10^{-10}	3.09×10^{-9}	4.48×10^{-9}
Non Carcinogenics	CTUh	1.88×10^{-9}	3.10×10^{-9}	7.19×10^{-9}	7.76×10^{-9}	6.47×10^{-9}	6.86×10^{-9}	3.17×10^{-8}	4.39×10^{-8}
Respiratory effects	kg PM2.5-eq	8.65×10^{-6}	9.31×10^{-6}	1.10×10^{-5}	1.13×10^{-5}	1.08×10^{-5}	1.11×10^{-5}	2.12×10^{-5}	2.96×10^{-5}
Ecotoxicity	CTUe	4.80×10^{-2}	7.85×10^{-2}	1.83×10^{-1}	1.97×10^{-1}	1.64×10^{-1}	1.74×10^{-1}	6.19×10^{-1}	8.67×10^{-1}
Fossil fuel depletion	MJ surplus	1.32×10^{-1}	1.94×10^{-1}	3.90×10^{-1}	4.18×10^{-1}	3.56×10^{-1}	3.76×10^{-1}	5.12×10^{-1}	7.56×10^{-1}

least 90 % of the total emissions across the PDD designs. The GWPs for the PSG, PG-INGR, and PG-ENGR designs with CCS were 53.6 %, 38.4 %, and 51.6 % higher than that of conventional petroleum derived diesel, and 34.8 %, 21.5 %, and 33 % higher than that of oil sands derived diesel, respectively (Fig. 5). Of course, there is no need to emphasize the GWP of the PDD plants when operated without CCS, as it is already evident. The emission of nitrogen oxides (NOx) and volatile organic compounds (VOC) throughout the life cycle of the PDD process contributes to smog formation (SF) in the atmosphere. The SF of the PDD designs, both with and without the use of CCS, are fairly similar. Nevertheless, the PDD designs has a SF tendency which is lower than the conventional petroleum and oil sands derived diesel plants by 33 % and 60.6 % respectively. The AP of the PDD plants is mainly due to the natural gas combustion to satisfy the plant utility requirements. The AP tendency of the PSG design with CCS was 57.6 % and 22.8 % higher than that of the PG-INGR and PG-ENGR designs, respectively due to higher utility requirement of this design (Okeke and Adams, 2018). While all the AP of all the PDD designs were worse compared to the conventional petroleum, the PG-INGR with CCS has an AP that is 21.7 % lower than that of oil sands derived diesel.

Eutrophication potential (EP) refers to the tendency of a water body to become saturated with excessive levels of nutrients, such as nitrogen and phosphorus, which are usually released by various human and industrial activities. As can be seen in Fig. 5, the PDD configurations had lower EP tendencies than the oil sands and conventional diesel processes of which the EP tendency of the PDD plants became even smaller when CCS was not used. Both the PG-INGR and PG-ENGR designs had higher EP due to natural gas consumed in the process compared to PSG design that processed only petcoke. With regards to carcinogenic (CP) and non-carcinogenic (NCP) potentials, all PDD designs showed impacts that were two orders of magnitude lower than those of the reference substances. As such, CP and NCP will not be discussed further in this work. The RE of the PSG design with CCS showed to be 17.7 % and 16.2 % lower than the PG-INGR and PG-ENGR designs with CCS respectively due to the emissions emanating from the natural gas consumed in the latter processes as feedstock.

When compared to the conventional and oil sands reference cases, the RE of the PDD processes is lower by at least 56.1 % and 68.5 % respectively. In addition, the ETPs of the three PDD configurations with CCS were found to be 87.3 %, 68.1 %, and 71.9 % lower than that of

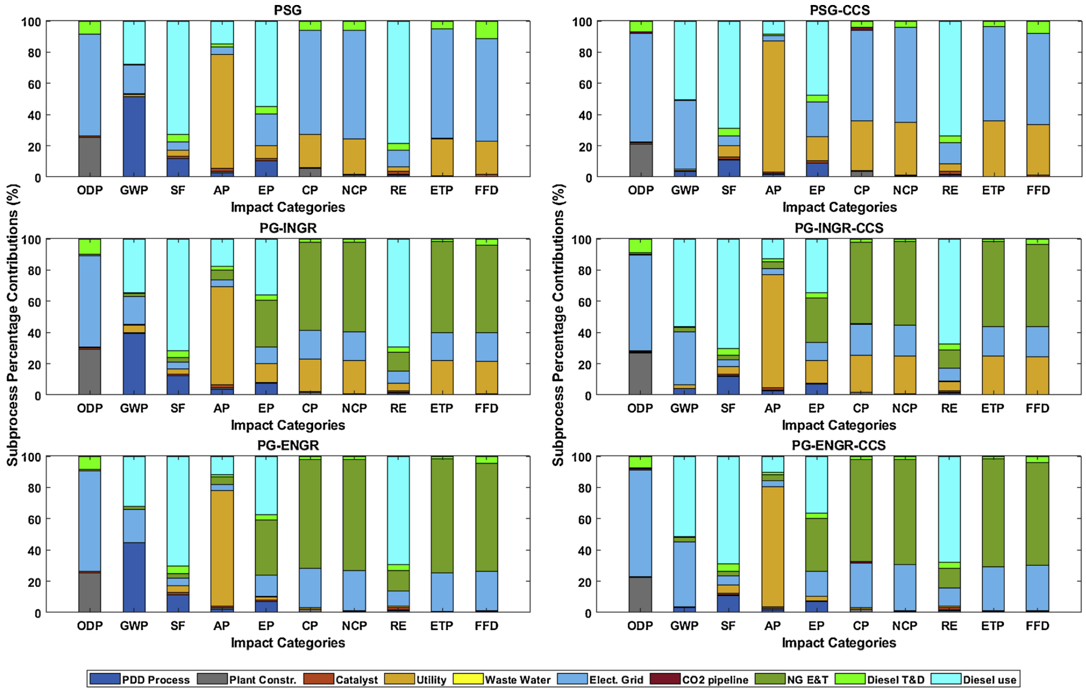

Fig. 4. Contribution plots of the WTW life cycle emissions for the PSG, PG-INGR, and PG-ENGR designs with and without CCS, located in Alberta.

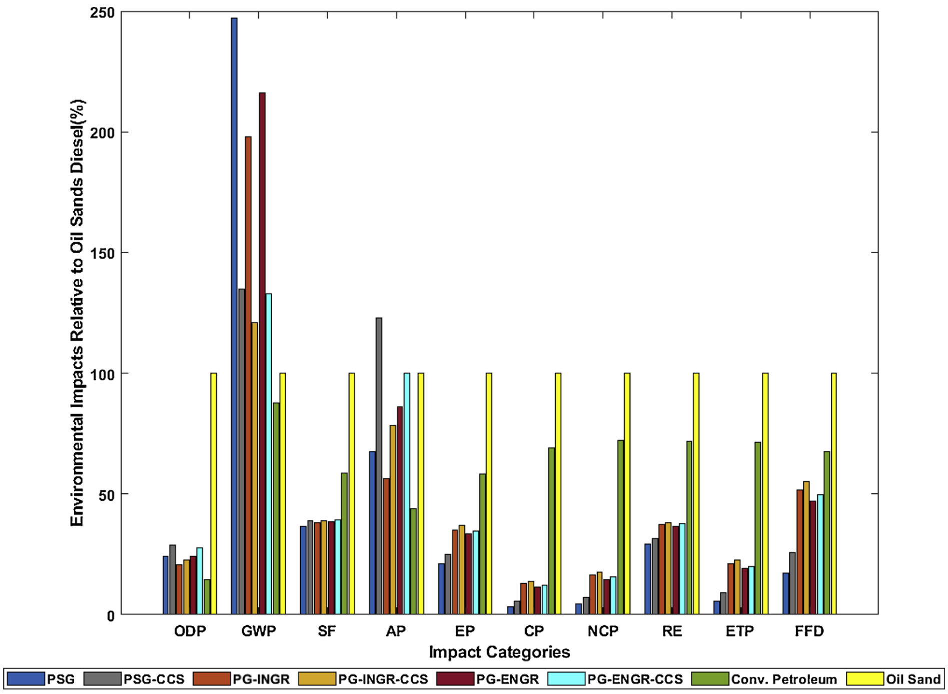

Fig. 5. Comparative WTW life cycle impact categories of the PSG, PG-INGR, and PG-ENGR with and without CCS relative to oil sands derived diesel for the Alberta plants.

Table 7
WTW inventory data for the PDD process designs with and without CCS in the Ontario location.

Inventory	PSG	PSG-CCS	PG-INGR	PG-INGR-CCS	PG-ENGR	PG-ENGR-CCS
Input flows (kg unless otherwise specified)						
Petcoke	0.300	0.300	0.183	0.183	0.206	0.206
Natural gas, in ground	0.041	0.049	0.061	0.071	0.080	0.086
Uranium, raw	1.20×10^{-8}	1.52×10^{-8}	9.22×10^{-9}	1.08×10^{-8}	1.17×10^{-8}	1.40×10^{-8}
Hydro (MJ)	0.080	0.101	0.061	0.072	0.078	0.094
Other renewables (MJ)	1.14×10^{-1}	1.45×10^{-1}	8.81×10^{-2}	1.03×10^{-1}	1.12×10^{-1}	1.34×10^{-1}
Other fuels (MJ)	1.66×10^{-3}	2.11×10^{-3}	1.28×10^{-3}	1.50×10^{-3}	1.63×10^{-3}	1.95×10^{-3}
River water, in river	2.54	2.84	0.65	0.95	1.33	1.44
Iron ore, raw	2.46×10^{-6}	6.80×10^{-5}	2.46×10^{-6}	6.80×10^{-5}	2.46×10^{-6}	6.80×10^{-5}
Aluminium ore, raw	1.51×10^{-6}	1.51×10^{-6}	1.51×10^{-6}	1.51×10^{-6}	1.51×10^{-6}	1.51×10^{-6}
Output flows						
Products flow						
Distance driven (km)	1	1	1	1	1	1
Gasoline (MJ_{HHV})	1.224	1.224	1.224	1.224	1.224	1.224
Sulfur (kg)	0.017	0.017	0.010	0.010	0.012	0.012
Sequestered CO_2 (kg)	0	0.584	0	0.353	0	0.439
Emissions flow to air (kg)						
Ammonia	8.88×10^{-8}	9.14×10^{-8}	5.87×10^{-8}	5.97×10^{-8}	6.57×10^{-8}	6.63×10^{-8}
Carbon dioxide	7.15×10^{-1}	2.79×10^{-1}	5.71×10^{-1}	2.87×10^{-1}	6.02×10^{-1}	2.82×10^{-1}
Carbon monoxide	2.54×10^{-3}	2.55×10^{-3}	2.52×10^{-3}	2.52×10^{-3}	2.52×10^{-3}	2.52×10^{-3}
Dintrogen monoxide	9.93×10^{-7}	9.93×10^{-7}	8.48×10^{-7}	8.48×10^{-7}	8.81×10^{-7}	8.81×10^{-7}
Methane	5.91×10^{-5}	6.14×10^{-5}	1.03×10^{-4}	1.04×10^{-4}	9.57×10^{-5}	9.57×10^{-5}
Nitrogen dioxide	1.80×10^{-7}	1.84×10^{-7}	1.93×10^{-7}	1.95×10^{-7}	1.80×10^{-7}	1.83×10^{-7}
Nitrogen oxides	4.98×10^{-4}	5.03×10^{-4}	3.70×10^{-4}	3.70×10^{-4}	3.96×10^{-4}	3.96×10^{-4}
NMVOC, Non-methane volatile organic compounds	2.11×10^{-5}	2.13×10^{-5}	1.33×10^{-5}	1.34×10^{-5}	1.49×10^{-5}	1.50×10^{-5}
Particulates, $> 2.50\,\mu m$, and $< 10\,\mu m$	8.68×10^{-6}	8.92×10^{-6}	5.58×10^{-6}	5.68×10^{-6}	6.27×10^{-6}	6.34×10^{-6}
Sulfur dioxides	1.73×10^{-5}	2.15×10^{-5}	1.80×10^{-5}	1.99×10^{-5}	1.08×10^{-5}	1.11×10^{-5}
Sulfur oxides	4.13×10^{-4}	8.22×10^{-4}	2.86×10^{-4}	4.46×10^{-4}	5.12×10^{-4}	6.17×10^{-4}
VOC, volatile organic compounds	1.14×10^{-4}	1.27×10^{-4}	1.11×10^{-4}	1.16×10^{-4}	1.18×10^{-4}	1.21×10^{-4}

conventional diesel, and 91 %, 77.2 %, and 79.9 % lower than that of oil sands diesel, respectively. Furthermore, Fig. 5 clearly shows that the conventional and oil sands diesel processes leads to higher FFD than the proposed PDD designs. Even when the FFD of the PG-INGR design which causes the most FFD among the PDD processes was compared to conventional and oil sands diesel processes, an 18.3 % and 44.7 % reduction was observed respectively. Thus, despite their high GWP, these PDD designs remain promising pathways that can allow stockpiled petcoke to be disposed of by converting it into diesel.

4.2. PDD plants: Ontario location

4.2.1. Life cycle inventories and midpoint impacts

Table 7 presents the life cycle inventory and emissions for the WTW assessment of the PDD plants located in Ontario. It is worth noting that the same amounts of petcoke and natural gas were consumed in both locations.

As shown in the system boundary, the main differences between the two locations were the impacts of transporting the petcoke from Alberta to Ontario and the emissions of their respective electricity grids. Thus, the life cycle CO_2 emissions of the PSG design operating with CCS in this location were 279 g/km distance driven, which is 40.2 % lower than the PSG for the Alberta location. Similarly, life cycle CO_2 emissions for the PG-INGR and the PG-ENGR designs with CCS were 287 and 282 gCO_2-eq/km distance driven, respectively. Unlike the Alberta plants, which differed significantly in terms of life cycle CO_2 emissions, none of the three designs operating with CCS in Ontario were clearly superior with respect to CO_2 emissions reduction. Although the Ontario location had lower life cycle CO_2 emissions, all the PDD designs produced higher levels of carbon monoxide, methane, NOx, and VOC due to petcoke transportation emissions. Thus, this work intends to present and analyze the overall environmental benefits of such trade-offs in plant location.

Table 8 shows the midpoint impact categories of the plants in Ontario. Due to the low grid carbon intensity at this location, plant construction, petcoke transport, and diesel transportation and distribution (T&D) are primarily the source of ODP (Fig. 6). When CCS was employed, the PSG, PG-INGR, and PG-ENGR designs at the Ontario location had GWPs that were 40 %, 31.2 %, and 38.4 % lower than those of the Alberta plants, respectively. Interestingly, the PSG design with CCS at the Ontario location had WTW GHG emissions of 281 gCO_2-eq/km distance driven which slightly outperformed the PG-INGR and PG-ENGR designs by 3 % and 1 %, respectively. This is because the PSG design consumed more electricity than the PG-INGR and PG-ENGR designs of which it is a huge contributor (44 %) to GHG emissions at the Alberta location. However, at this location, the electricity grid GHG emission is minimal (2 %), thus resulting to a reduced total GHG emission. Furthermore, the PSG design was able to reduce GHG emissions by 8 % and 19 % compared conventional petroleum and oil sands derived diesel, respectively (Fig. 7). Although the PG-INGR and PG-ENGR with CCS designs consumed natural gas, at least 29.2 % and 41.8 % reduction in FFD was achieved when compared to conventional and oil sands diesel respectively. This reduction in GHG emissions not only demonstrates that the proposed PDD configurations offer an environmentally friendly petcoke disposal pathway, but, most importantly, it highlights petcoke's potential as a feedstock for diesel production. Although this study did not consider the credits accrued from displacing more oil sand or conventional petroleum extraction for diesel fuel production, the benefits of such approaches can further offset the emissions of PDD processes.

Except for FFD, it is unsurprising to notice the increase in other impact categories due to the emissions accrued during the transportation of the petcoke to Ontario. The increase in the environmental impacts of the PDD designs illustrates how a trade-off between GHG emissions savings and increase in the emissions of other impact categories must me made for plants located in Ontario. Compared to the plants located in Alberta, the PSG, PG-INGR, and PG-ENGR plants in Ontario were able to reduce FFD by 39.6 %, 13.3 %, and 20.8 % when operated with CCS, respectively. However, considering the impact of the grid only, there is up to 88.2 % reduction in FFD for the plants located in Ontario compared to Alberta. This is not surprising as the Alberta electricity grid is still almost exclusively dependent on fossil fuels. Overall, the environmental benefits of locating a plant within a low carbon intensive electricity grid, such as Ontario, are clearly evidenced by the reduced FFD, which directly correlates to reduced GHG emissions. Thus, it can be concluded that an electricity grid which is less dependent of fossil sources like Ontario's is most desirable when attempting to build a PDD plant. To make a decision of which of the PDD designs with CCS to build in Ontario based on GHG emissions (at least due to the attention GWP has received in recent years), the choice of which plant to adopt is not clear given the negligible difference in GHG emissions among the designs. Thus, an important metric that compares the cost invested to avoid CO_2 emissions termed cost of CO_2 avoided (CCA) (Adams et al., 2017) is computed to aid in the decision making.

4.3. Cost of CO_2 avoided

In this study, the cost of CO_2 avoided (CCA) defined as the difference in the minimum diesel selling price (MDSP) of the PDD process compared to a "status quo" reference process (oil sands derived diesel) divided by the difference in emissions between both processes as shown by Eq. 1:

$$\frac{MDSP_{PPD} - MDSP_{Ref}}{GWP_{Ref} - GWP_{PPD}} \tag{1}$$

where $MDSP_{PPD}$ and GWP_{PPD} are the minimum diesel selling price and WTW GWP of the PDD plants while $MDSP_{Ref}$ and GWP_{ref} are the minimum diesel selling price and WTW GWP of the oil sands diesel process respectively.

Most of the detailed costs data for the calculation of the CCA can be found in our economics work (Okeke and Adams, 2018). In this study,

Table 8
WTW LCA results for the petcoke to diesel plant located in Sarnia, Ontario, for a basis of 1 km distance driven.

Impact categories	Units	PSG	PSG-CCS	PG-INGR	PG-INGR-CCS	PG-ENGR	PG-ENGR-CCS	Conv. Diesel	Oil Sand Diesel
Ozone depletion	kg CFC-11-eq	1.57×10^{-12}	1.61×10^{-12}	1.39×10^{-12}	1.41×10^{-12}	1.43×10^{-12}	1.45×10^{-12}	1.79×10^{-12}	1.22×10^{-11}
Global warming	kg CO_2-eq	7.17×10^{-1}	2.81×10^{-1}	5.75×10^{-1}	2.91×10^{-1}	6.06×10^{-1}	2.85×10^{-1}	3.05×10^{-1}	3.48×10^{-1}
Smog	kg O_3-eq	1.29×10^{-2}	1.31×10^{-2}	9.68×10^{-3}	9.76×10^{-3}	1.04×10^{-2}	1.04×10^{-2}	7.02×10^{-3}	1.20×10^{-2}
Acidification	kg SO_2-eq	7.52×10^{-4}	1.17×10^{-3}	5.71×10^{-4}	7.33×10^{-4}	8.12×10^{-4}	9.17×10^{-4}	3.33×10^{-4}	7.59×10^{-4}
Europhication	kg N-eq	2.21×10^{-5}	2.31×10^{-5}	2.12×10^{-5}	2.17×10^{-5}	2.15×10^{-5}	2.16×10^{5}	2.01×10^{-5}	3.60×10^{-5}
Carcinogenics	CTUh	2.29×10^{-10}	2.96×10^{-10}	5.97×10^{-10}	6.30×10^{-10}	5.31×10^{-10}	5.41×10^{-10}	3.09×10^{-9}	4.48×10^{-9}
Non Carcinogenics	CTUh	2.26×10^{-9}	3.03×10^{-9}	7.16×10^{-9}	7.56×10^{-9}	6.27×10^{-9}	6.34×10^{-9}	3.17×10^{-8}	4.39×10^{-8}
Respiratory effects	kg PM2.5-eq	1.25×10^{-5}	1.28×10^{-5}	1.32×10^{-5}	1.33×10^{-5}	1.31×10^{-5}	1.32×10^{-5}	2.12×10^{-5}	2.96×10^{-5}
Ecotoxicity	CTUe	4.80×10^{-2}	6.78×10^{-2}	1.77×10^{-1}	1.87×10^{-1}	1.53×10^{-1}	1.55×10^{-1}	6.19×10^{-1}	8.67×10^{-1}
Fossil fuel depletion	MJ surplus	7.80×10^{-2}	1.17×10^{-1}	3.43×10^{-1}	3.63×10^{-1}	2.95×10^{-1}	2.98×10^{-1}	5.12×10^{-1}	7.56×10^{-1}

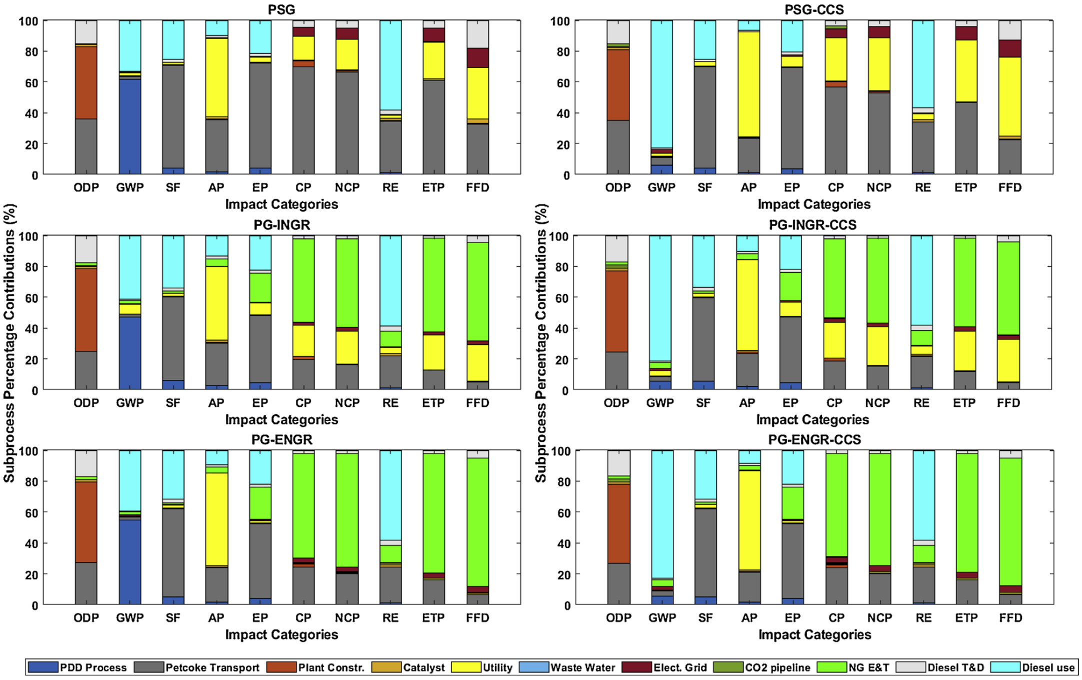

Fig. 6. Contribution plots of the WTW life cycle emissions of the PSG, PG-INGR, and PG-ENGR designs with and without CCS, located in Ontario.

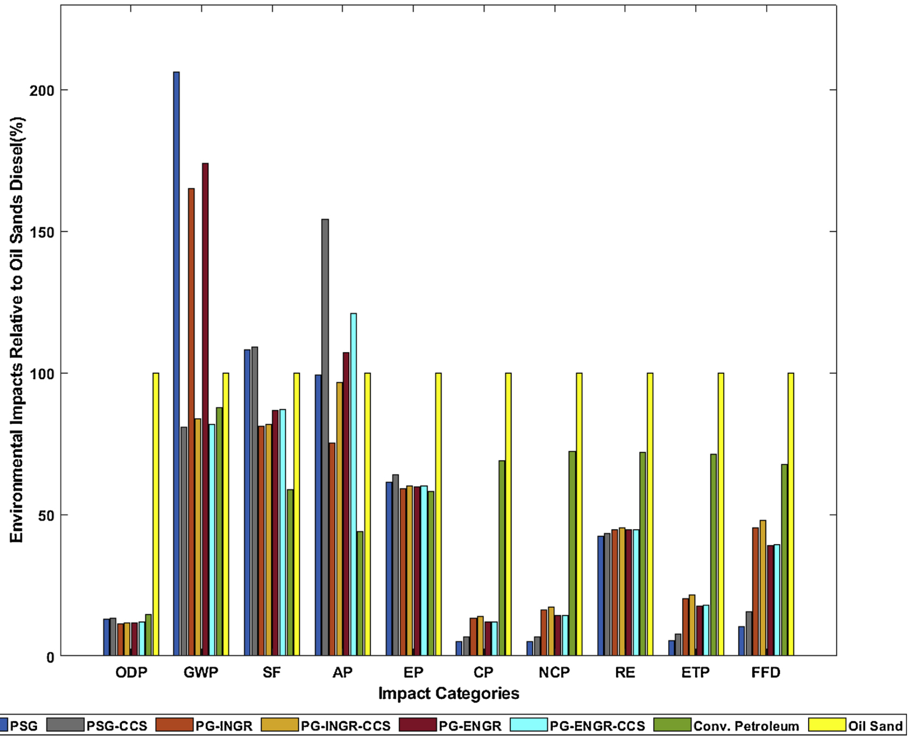

Fig. 7. Comparative WTW life cycle impact categories of the PSG, PG-INGR, and PG-ENGR with and without CCS relative to oil sands derived diesel for the Ontario plants.

Table 9
CCA calculation for the three PDD plants with CCS enabled.

	PSG	PG-INGR	PG-ENGR
Total capital investment (M$)	1174	1176	1172
Operating Cost (M$/yr)	320	362	358
MDSP ($/GJ)	15.0	12.6	14.2
WTW GWP (kgCO$_2$-eq/GJ)	85.2	88.1	85.9
CCA ($/tonneCO$_2$-eq)	243	144	213

we used the cost estimates from the prior work, but then in this work we included additional information such as the capital (CAPEX) and operating (OPEX) costs of the hot utilities generation and its flue gas CO$_2$ capture system (including compression to 153 bar). In addition, petcoke transportation and CO$_2$ sequestration costs of $5.92 per tonne (EIA, 2017a) and $13.82 per tonne (Rubin et al., 2015) in 2017 US dollars respectively were used. For the reference plant, the MDSP was estimated to be $10.1 per GJ$_{HHV}$ using the 2017 average refinery diesel wholesale price (EIA, 2017b) with an assumed $1.6 per GJ$_{HHV}$ refinery margin while the WTW GWP was 105 kgCO$_2$-eq/GJ$_{HHV}$ diesel driven.

As can be seen in Table 9, although the PG-INGR design showed to have the highest GWP, its CCA 40.9 % and 32.7 % lower than the PSG and PG-ENGR designs respectively. Thus, when the GWP and CCA of the proposed PDD designs are considered, the PG-INGR design showed to most the viable configuration.

4.4. Sensitivity analysis

This section presents a sensitivity analysis of the key parameters that were used in conducting the LCA in order to ascertain which parameters are most critical to the system's performance. Specifically, sensitivity analyses were performed for GWP and FFD for the Ontario plants with CCS, as these plants had the lowest environmental impacts for these categories. The studied parameters were transport distance, electricity consumption, and vehicle fuel economy as they are the parameters which have significant impact on GHG and FFD compared to other parameters. In addition, we evaluated the overall effect of petcoke waste assumption that assumes no indirect emission by imposing a wide range of emissions on petcoke. Finally, we also carried out a sensitivity analysis on the effects of petcoke transportation cost, CO$_2$ sequestration cost, debit-to-equity (D/E) ratio, internal rate of return (IRR), and CO$_2$ emission tax on cost of CO$_2$ avoided (CCA). During the analysis, one parameter was manipulated, while all other parameters were kept constant. Fig. 8(a) shows how GHG emissions are affected by a 20 % increase or decrease in the parameters. Unsurprisingly, a 20 % decrease in vehicle fuel economy resulted in a WTW GWP of 338 gCO$_2$-eq/km distance driven.

In a situation where the PDD diesel is used in a vehicle with improved fuel economy, the GWP dropped to 225 gCO$_2$-eq/km distance driven. Between petcoke transport distance and electricity, the former showed to have lower effect on GWP when increased or decreased by 20 %. Similarly, the effect of these parameters on FFD was also examined, as is shown in Fig. 8(b). When the fuel economy of the passenger vehicle is reduced by 20 %, it increases FFD to 141 MJ surplus per km distance driven as more resources is consumed to achieve the same distance driven whereas at an improved vehicle fuel economy, a 93.6 MJ surplus per km distance driven was recorded. Overall, it showed that the WTW of PDD is largely dependent on the type of vehicle used.

As shown in Fig. 9(a), compared to the PSG design, which had a GWP of 338 gCO$_2$-eq/ km distance driven when vehicle fuel economy was decreased by 20 %, the PG-INGR design showed a GWP of up to 349 gCO$_2$-eq/km distance driven. In addition, increasing or decreasing electricity consumption and petcoke travel distance did not improve the PG-INGR design in terms of GHG emissions and FFD (Fig. 9(b)) in comparison to the PSG design.

As shown in Fig. 10(a), decreasing vehicle fuel economy for the PG-ENGR design caused the GWP to increase to 342 gCO$_2$-eq/km distance driven from the base case value of 285 gCO$_2$-eq/km distance driven. Regardless, this 20 % drop in vehicle fuel economy still resulted in GWPs for the three proposed designs that were lower than the GWP for oil sands-derived diesel, which had WTW GHG emissions in the range of 357–1179 gCO$_2$-eq/km distance driven. Similarly, a lower depletion of fossil resources is observed when the vehicle fuel economy was improved as depicted in Fig. 10(b) with electricity consumption and petcoke transport distance having little effects.

As shown in Fig. 11 and with an estimated petcoke indirect emission between 30 and 165 gCO$_2$-eq/kg (based on an approximate calculation

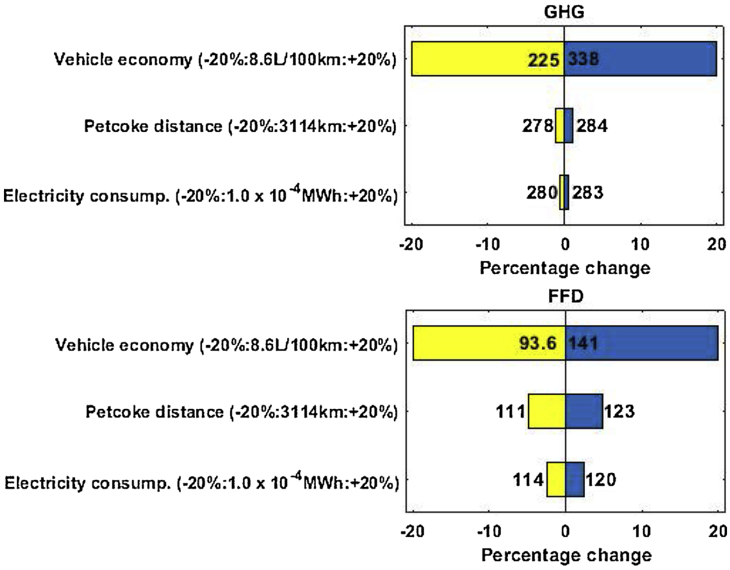

Fig. 8. Sensitivity analysis of key parameters on (a) GHG emissions, (b) and FFD for the PSG design located in Ontario.

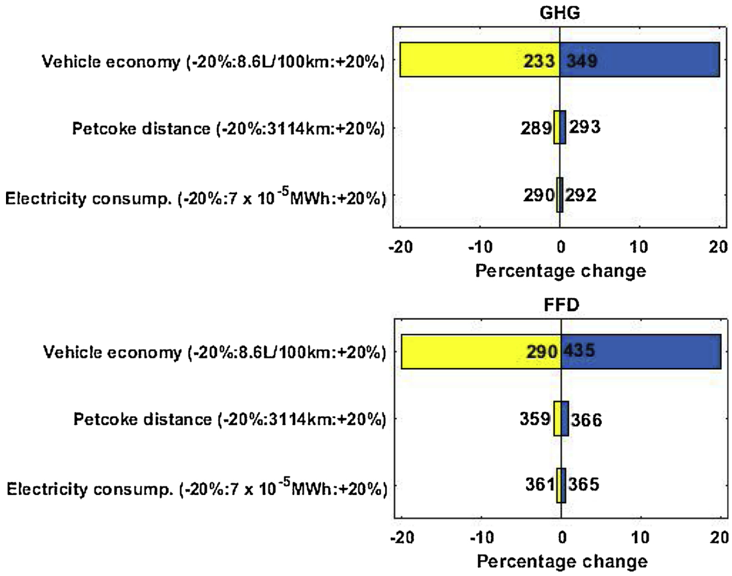

Fig. 9. Sensitivity analysis of key parameters on (a) GHG emissions, and (b) FFD for the PG-INGR design located in Ontario.

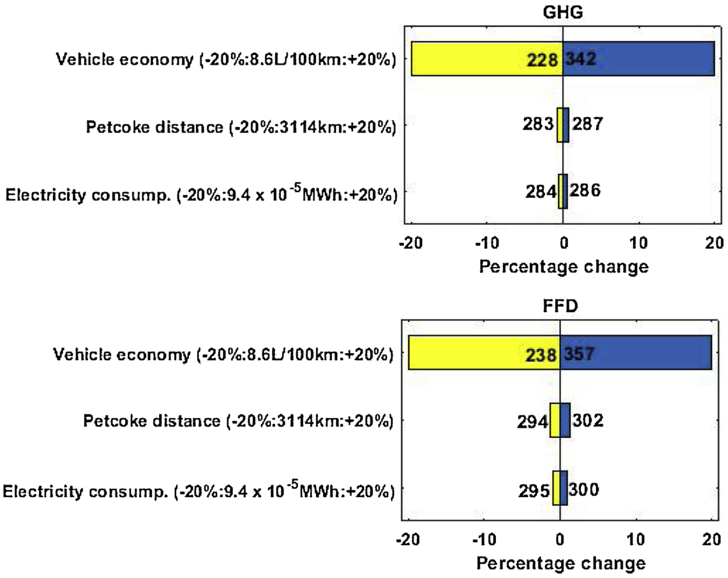

Fig. 10. Sensitivity analysis of key parameters on (a) GHG emissions, and (b) FFD for the PG-ENGR design located in Ontario.

of a refinery that produces gasoline, diesel, and petcoke and emission allocation of 30 %, 65 %, and 5 % (Okeke and Adams, 2018)), petcoke indirect emission can increase the WTW GHG emission of the PSG, PG-INGR, and PG-ENGR up to a maximum of 331, 321, and 319 gCO_2-eq/km traveled. Even though this represents about 8.6 % increase in GHG emissions compared to the conventional petroleum, an 8.3 % reduction is recorded when compared to the oil sands diesel. Furthermore, the sensitivity analysis of the effect of cost parameters on CCA was examined in Fig. 12. It can be concluded that the IRR has the most impact on CCA followed by D/E ratio and CO_2 sequestration cost. At a maximum CCA of $289/ t$CO_2$-eq estimated for the PSG design at IRR of 15 %, it is still lower than the CCA of a bio-ethanol process which is about $227 to 680/t$CO_2$-eq (Sims et al., 2008; CBO, 2010).

5. Conclusions

This paper has presented the results of an environmental impact assessment of six novel processes that combine petcoke gasification and natural gas reforming to produce diesel. The scope of analysis for this assessment included the direct and indirect material and energy inputs, along with their associated products and emissions. A total of three designs in both high (Alberta) and low (Ontario) electricity grid

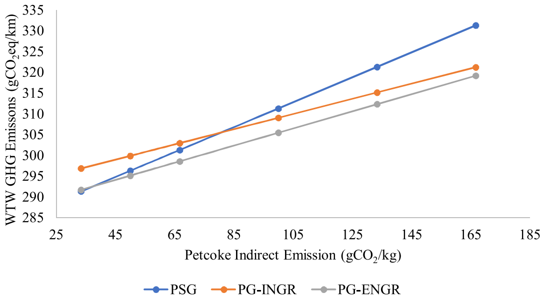

Fig. 11. Sensitivity analysis of the effect of petcoke indirect emission on the WTW GHG emissions.

emissions locations were studied with and without carbon capture and sequestration technology in order to ascertain how design and location affect overall life cycle environmental performance.

For the Alberta location, the PSG, PG-INGR, and PG-ENGR designs without CCS released up to 860, 688, and 750 gCO_2-eq/km distance driven, respectively; when CCS technology was incorporated, these figures dropped to 469, 423, and 463 gCO_2-eq/km distance driven.. However, the WTW GHG emissions for the PSG, PG-INGR, and PG-ENGR designs in Ontario were 281, 291, and 285 gCO_2-eq /km distance driven when operated with CCS. As all CCS plants in Ontario had almost equal GHG emissions, the cost of running each design (CCA) was considered which showed that the PG-INGR is more economically feasible, with a best case CCA of about $144/tonne. This CCA is low enough to make it an attractive option for strictly GHG reduction purposes compared to other transportation fuel GHG-reduction efforts such as bioethanol of about $227 to 680/$tCO_2$-eq (Sims et al., 2008; CBO, 2010), fermentation-based bio-butanol of about $470 to 900/ tCO_2-eq (Dalle Ave and Adams, 2018), or thermochemical bio-butanol of about $130 to 265/ tCO_2-eq (Okoli and Adams, 2017).

Moreover, each of the proposed designs had a lower FFD than the conventional petroleum and oil sands diesel processes, both with and without the use of CCS technology. For all other studied environmental impacts, the proposed designs had lower environmental impacts at least when compared to the oil sands diesel processes when CCS was used. Hence, this analysis demonstrates that the proposed petcoke conversion strategies provide WTW GHG emissions levels that are competitive with those of the conventional petroleum-derived diesel process, and superior to those of the oil sands process.

Future work will include a comparative environmental impact assessment of processes that convert petcoke to electricity, as well an environmental impact assessment of the status quo (petcoke stockpiling). The findings of such research will help inform stakeholders about the potential benefits and trade-offs offered by disposing of petcoke via power production or liquid fuels production instead of stockpiling.

CRediT authorship contribution statement

Ikenna J. Okeke: Conceptualization, Methodology, Data curation, Writing - original draft, Formal analysis. **Thomas A. Adams:** Supervision, Investigation, Funding acquisition, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

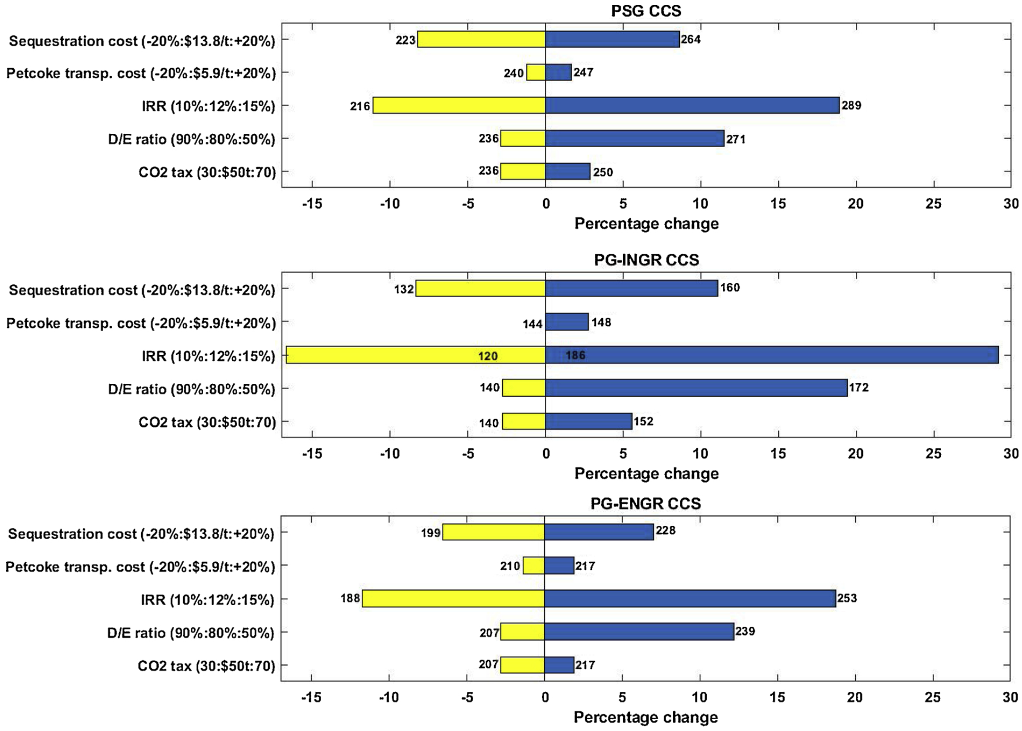

Fig. 12. Sensitivity analysis on the effects of petcoke transportation cost, CO_2 sequestration cost, D/E ratio, IRR, and CO_2 tax on cost of CO_2 avoided (CCA).

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.ijggc.2020.103012.

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Chapter 4

Application of petroleum coke disposal to electricity generation: cost and environmental impact assessment of petroleum coke IGCC power plant.

The content of this chapter is the **published reprint** of the following conference proceedings after peer-review,

Okeke, Ikenna J., and Thomas A. Adams II. "Systems Design of A Petroleum Coke IGCC Power Plant: Technical, Economic, And Life Cycle Perspectives." Computer Aided Chemical Engineering. Vol. 47. Elsevier, 2019. 163-168.

SYSTEMS DESIGN OF A PETROLEUM COKE IGCC POWER PLANT: TECHNICAL, ECONOMIC, AND LIFE CYCLE PERSPECTIVES

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Abstract

The petroleum coke gasification integrated gasification combined cycle power plant (petcoke-IGCC) is a promising avenue for disposal of the ever-growing amount of stockpiled petroleum coke. In this work, we present a novel techno-economic and life cycle assessment of the process operated with carbon capture and sequestration. The proposed petcoke-to-electricity plant is designed and simulated in Aspen Plus v10. The proposed power plant was compared against coal integrated gasification combined cycle (coal-IGCC) and supercritical pulverized coal power plants operated with carbon capture and sequestration. The results showed that although the efficiency of the coal-IGCC plant is higher than the petcoke-IGCC plant, the higher energy density of the petcoke and lower resource costs were such that the levelized cost of electricity of petcoke-IGCC was lower than coal-IGCC. Furthermore, the feed flow rate of petcoke to the petcoke-IGCC process is approximately 14% lower than the coal feed rate to coal-IGCC in order to produce the same net electric power. In addition, the life cycle greenhouse gas emissions and fossil fuel depletion of the petroleum coke integrated gasification combined cycle power were around 43% and 45% lower than the supercritical pulverized coal power plants respectively. Overall, the proposed petroleum coke power plant showed to be a feasible avenue by which an environmentally safe "end of life" of petroleum coke can be achieved.

Keywords

Petroleum coke, Gasification, Electricity, CO_2 capture, Life cycle assessment.

Introduction

Large amounts of petroleum coke (petcoke) resulting from heavy crude oil refining has been stockpiled in Canada, which has raised concerns for its means of disposal. Traditionally, petcoke that is unsuitable as metallurgical resource is combusted to either generate electricity or to produce steam needed in the refinery. However, with government regulations that restricts the combustion of petcoke (Stockman 2013), the integrated gasification combustion cycle (IGCC) may be a feasible alternative. The question is if petcoke gasification (similar to coal) for power generation can serve as a better disposal approach with reduced environmental impacts and viable economic incentives compared to permanent stockpiling.

Contrary to mature coal and natural gas processes for power generation, utilizing petcoke in a dedicated IGCC process has received limited attention. However, some studies have explored avenues by which petcoke can be disposed. For instance, Washbash River power plant explored the technical feasibility of a petcoke-IGCC plant for which they found the performance to be comparable to coal-IGCC (Amick 2000). In 2013, the National Energy Research Laboratory (NETL) carried out an economic assessment of a petcoke fueled power plant and showed that

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the process can compete in the market when the petcoke price is free (Kramer 2003). Similarly, the cost performance of a petcoke gasification to power and hydrogen process was studied by (Orhan, Mcapline et al. 2014) showing that it is more profitable to produce only electric power instead of a combination of power and hydrogen. Recently, the feasibility of integrating petcoke gasification into to a steam assisted gravity drainage facility for a bitumen upgrading was studied by (Lazzaroni, Elsholkami et al. 2017) as a petcoke disposal pathway. The study found that up to 37% of the required steam can be satisfied by the use of petcoke, hence reducing natural gas usage. However, none of these studies presented a comprehensive life cycle assessment to ascertain whether it is environmentally desirable.

Therefore, this paper presents the technical, economic, and cradle-to-gate (CTG) life cycle assessment of a potential IGCC power plant with carbon capture and sequestration (CCS) based on petcoke. It is compared against coal-IGCC with CCS and supercritical pulverized (SCPC) with CCS power plants. SCPC w/CCS is chosen as the status quo process for comparison purposes because it is the most advanced type of power plant currently operating in Western Canada (SaskPower 2017) where the majority of Canadian petcoke production takes place. Coal-IGCC is also of technical interest for comparison purposes as the most advanced form of coal power recently constructed in the United States (Duke Energy) and a direct competitor to SCPC w/CCS.

Figure 1 depicts the process flow diagram and CTG system boundary of the proposed design. Petcoke is prepared in slurry form and is gasified using oxygen from an air separation unit (ASU) to produce syngas. The syngas contains impurities which is removed and then sent to the water-gas shift (WGS) process to raise the hydrogen ratio and convert the COS in the syngas. Containing high amount of CO_2 and H_2S, the syngas is sent to the acid gas removal (AGR) unit where the CO_2 is captured and compressed for sequestration while the H_2S is sent to the Claus unit for sulfur production. Finally, electricity is generated by combusting the clean syngas in a gas turbine while the flue gas (before being flare to the environment) heat is recovered in a heat recovery steam generator (HRSG) used to generate high pressure steam which is expanded in a steam turbine for additional power generation.

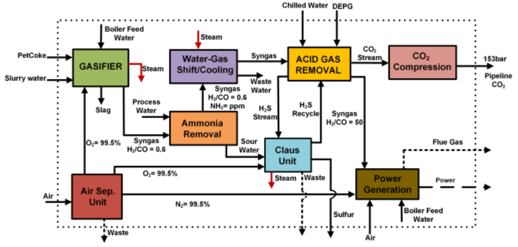

Figure 1. Process flow diagram and CTG system boundary of the proposed petcoke-IGCC power plant

Methodology

Process model physical properties and assumptions

In this work, delayed petcoke was used as the feed to the IGCC plant. For comparison purposes, all plants are sized for a net power output of 550 MWe. The properties of the delayed coke as compared to that of bituminous coal are shown in table 1.

Process simulations of the petcoke-IGCC plant were carried out in Aspen Plus v10 using a combination of physical property models due to the complexity of each subprocess in the overall system. The Peng-Robinson with Boston-Mathias alpha function (PR-BM) was used widely in the flowsheet to be consistent with our previous work (Okeke and Adams II 2018). Due to the very high pressure of operation at the CO_2 compression section of the process, the Predictive Redlich-Soave (PSRK) model was used in this section as it has shown to perform accurately at high pressures (Adams and Barton 2010). As expected, the STEAMNBS was used to model the steam combined cycle subprocesses. The property packages for modeling the Claus unit and Selexol process for sulfur production and the removal of H_2S and CO_2 respectively were electrolyte non-random two liquid (ELECNRTL) activity coefficient and the perturbed-chain statistical associated fluid theory (PC-SAFT) consistent with the validated work of (Field and Brasington 2011).

Thermophyical properties of the chemical species considered in the simulations used the Aspen Plus APV100 Pure 36 and Solids databases for the conventional components. The non-conventional substance, petcoke, was specified as a pseudo-component with properties described in table 1.

Process description

Delayed petcoke is crushed and mixed to form slurry which is fed to the petcoke gasifier modeled as the Wabash E-Gas (Amick 2000). The gasifier was designed to operate at 1426 °C and 56 bar in the presence of oxygen to produce syngas which typically contains carbon monoxide, carbon dioxide, and hydrogen with impurities such as carbonyl sulfide and ammonia. Oxygen required for the gasification process and for the entire system is provided via the ASU while the waste nitrogen is used as a diluent in the gas turbine to control its temperature.

The produced syngas is quenched to adiabatic saturation temperature of about 200 °C which enables the removal of entrained slag. Ammonia impurities are also removed using its very high solubility in water compared to other components in the syngas.

WGS is employed in order to convert carbonaceous energy in the syngas (CO) into carbonless energy (H_2). Both the high and low temperature WGS reactors were employed in order to overcome the equilibrium limitations of the high temperature process (Ratnasamy and Wagner 2009). The WGS reactions occurs in the presence of copper promoted iron-based and copper-zinc aluminum catalysts for the high and low temperature processes respectively (Twigg 1989). The WGS reaction was modeled using equilibrium reactors which proceeds following Eq. (1):

$$CO + H_2O \leftrightharpoons H_2 + CO_2 \qquad (1)$$

To ensure that the catalyst life and activity are maintained during the WGS reaction due to the presence of sulfur, the steam to carbon monoxide ratio is kept at 2:1 (Hendriks 2012). In addition to the carbon monoxide conversion, COS hydrolysis reaction is designed to convert 99% of COS in the presence activated alumina catalyst following Eq. (2):

$$COS + H_2O \leftrightharpoons H_2S + CO_2 \qquad (2)$$

High pressure acid gas removal using dimethyl ether polyethylene glycol (DEPG) was employed to remove H_2S and capture CO_2. These removals were achieved using the two-stage Selexol configuration which selectively absorbs H_2S and CO_2 in the H_2S and CO_2 absorbers respectively. First, syngas enters the H_2S absorber where H_2S is selectively removed, sent through the H_2S concentrator to remove CO_2 (enrich the H_2S stream) and is sent to the stripper. The enriched H_2S stream outlet of the stripper is subsequently sent to the Claus unit for sulfur production while the recovered lean solvent is sent to the CO_2 absorber. The lean solvent together with the semi-lean solvent are designed to capture 90% of the inlet CO_2. Pressure drops across a series of flash drums are used to regenerate the CO_2 rich Selexol which is sent back to the CO_2 absorber while the CO_2 rich stream is sent for compression. This work employed the two-stage Selexol Aspen Plus flowsheet of (Field and Brasington 2011).

Table 1. Delayed petcoke and bituminous coal properties

	Delayed[a] coke	Bituminous coal[b]
	Ultimate Analysis (wt %dry)	
C	84.9	71.72
H	3.9	5.06
N	1.3	1.41
S	6	2.82
Cl	0	0.33
Ash	3.1	10.91
O	0.8	7.75
	Proximate Analysis (wt %)	
Moisture	1.8	11.2
Volatile matter	11.9	34.99
Fixed carbon	83.3	44.19
Ash	3	9.7
HHV (MJ/kg)	34.7	27.1

a Data from (Watkinson, Cheng et al. 1989)
b Data from (Klara, Woods et al. 2007)

Compression of the captured CO_2 was carried out in stages to supercritical condition before pumping it to 153 bar designated for sequestration pipeline purposes.

The Claus process is employed to convert the H_2S from the acid gas removal section to sulfur. Since the H_2S recovered was at purities higher than 40 mol%, the split flow sulfur recovery process was employed (Jacobs). The process is primarily a partial oxidation of H_2S to yield SO_2 which further reacts to produce elemental sulfur as shown in Eq. (3) and (4)

$$H_2S + \frac{3}{2}O_2 \rightarrow SO_2 + H_2O \qquad (3)$$

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \qquad (4)$$

Being a high temperature process, the waste heat boiler is used to produce steam used to satisfy the process demands. 96% of process sulfur was recovered. For the life cycle assessment study, sulfur was taken as a co-product but no environmental credit for displacing petroleum-based sulfur was considered.

The clean syngas from the CO_2 capture unit is combusted in the presence of excess air (more than the stoichiometric ratio) that ensures complete combustion of the fuels at high temperature and pressure in an F-Class gas turbine to produce electricity. Air and waste N_2 from the ASU were used as a diluent in the combustion chamber of the turbine. The waste heat from the exhaust of the turbine is recovered via the HRSG which is used to generate high pressure steam to produce extra electricity in a steam cycle. The flue gas is vented through the stack to the atmosphere which accounts for the direct process emissions.

The overall process utility requirement is evaluated by carrying out a heat exchanger network design using Aspen Energy Analyzer to determine the minimum energy requirements and heat exchanger network costs. The net energy requirements are the system wide cooling and chilled water which were provided via the cooling tower and natural gas fired ammonia chiller respectively.

Cost Analysis

The estimation of the total capital investment (TCI) and operating costs (OPEX) of the proposed petcoke-IGCC power plant are based on the systems mass and energy balance. Each unit operations cost is evaluated using a combination of literature data and Aspen Plus Economic Analyzer to obtain the bare equipment cost of which indirect costs correlations (Peters, Timmerhaus et al. 2003) were employed to calculate the TCI. The OPEX consists of the variable and fixed operating costs, which were also estimated from the process consumables and the labor requirements respectively. The estimated costs are presented in $US2016 using the Chemical Engineering Plant Cost Indices (CEPCI) to be consistent with our previous study (Adams II, Hoseinzade et al. 2017). The LOCE which was used as a measure of the profitability was calculated using the following economic parameters presented in table 2.

Table 2. Economic assumptions

Parameter	Value	Parameter	Value
Plant life (yrs)		Tax Rate (%)	40
Plant avail. (%)	85	Rate of Return (%)	12
Plant loan (yrs)	30	Depreciation	MACRS
loan interest (%)	9.5	Working capital	5%
Debit/Equity (%)	50	Operating hours	8000

Life cycle assessment

The goal of this assessment is to compute the CTG environmental impacts of the proposed petcoke-IGCC plant. The scope and boundary of the petcoke-IGCC process is as shown in figure 1. For the inventory data scaled for a functional unit of 1 MWh net power output, the TRACI v2.1 endpoint method in SimaPro was used to quantify the impact categories of the respective processes. The impact categories considered were: ozone depletion potential (ODP), global warming potential (GWP), smog formation (SF), acidification potential (AP), eutrophication potential (EP), carcinogenic potential (CP), non-carcinogenic potential (NCP), respiratory effects (RE), ecotoxicity potential (ETP), and fossil fuel depletion (FFD). While the inventory data for the coal SCPC and IGCC plants were obtained from (Nease and Adams II 2015), that of the petcoke-IGCC plant was from our model as shown in table 3.

Table 3. CTG life cycle inventory

Inventory	Petcoke-IGCC
Input flows (kg unless otherwise specified)	
Petcoke	367
Catalyst, aluminum-based	0.34
Air	5792
Process water	330
Cooling water, cooling tower	1768
Waste water treatment (m^3)	884
Chilled water (GJ)	0.94
Output flows	
Product Flows	
Electricity (MWh), basis	**1**
Sulfur (kg)	21.5
Sequestered CO_2 (kg)	964
Emissions flows to air (kg)	
Carbon monoxide	0.06
Carbon dioxide	130.3
Water	570.5
Argon	71.3
Nitrogen dioxide	0.1
Nitrogen oxide	12.6
Sulfur dioxide	2.4×10^{-3}

Results

Systems performance

Table 4 shows the performance of the petcoke-IGCC power plant operating with CCS. This performance is compared against the traditional coal based IGCC power plant so as to ascertain if the proposed design offers any performance improvement.

As can be seen in table 3, for a net power output of 550 MWe, there is a 15% higher feed rate for the coal-IGCC plant compared to the petcoke-IGCC process. This is because of the larger heating value of petcoke compared to coal. As shown in table 1, the energy density of coal is 22% lower than that of petcoke. Hence, more coal (by mass) is required to achieve the same energy produced by petcoke.

But on the negative side, petcoke produces up to 10% more direct CO_2 emissions per unit energy produced (Stockman 2013). And given the high amount of sulfur present in petcoke, a high energy penalty is required to clean the syngas produced. Compared to the coal plant, the petcoke design has slightly higher auxiliary power requirement even for a reduced amount of feed inlet compared to the coal plant. As already mentioned, this is due to the extra parasitic load needed in the AGR unit to to remove the high sulfur and CO_2 in petcoke-derived syngas.

Table 4. Summary of the IGCC performance

Parameters	IGCC	IGCC[a,b]	SCPC[c]
CCS Enabled	Yes	Yes	Yes
Feed type	Petcoke	Coal	Coal
Feed rate (tonne/h)	200.6	235	225
Capture Solvent	Selexol	Selexol	Amine
Total Power (MW)	756	753	642
Aux. Power (MW)	206	203	91
Net Power (MW)	550	550	550
Thermal Eff. (HHV%)	26	31	33
Cold Gas Eff. (HHV%)	72.9	81	-
Heat Rate (MJ/MWh)	12,737	11,607	11,077
Unit Fuel Cost ($/GJ)	0.00	2.5	2.5
TCI ($M)	1780	1753	1784
LCOE ($/MWh)[d]	123.51	140.5	132.6
Direct GHG Emissions ($kgCO_2eq/MWh$)	130.3	98.5	97
Indirect GHG Emissions ($kgCO_2eq/MWh$)	64.5	151.6	191.8
Total GHG emissions ($tonneCO_2eq/MWh$)	0.196	0.251	0.286

a Source data from (Fout, Zoelle et al. 2015) for a 513 MWe output and a cost year of 2011 USD.

b Updated values for a 550 MWe net outpower with a 2016 cost.

c Source data from (Fout, Zoelle et al. 2015) for a 5550 MWe output and updated to 2016 USD cost

d Does not include transportation and storage cost.

Based on the aforementioned, the efficiency of the petcoke-IGCC design is 5% points lower than that of coal-IGCC. Two other parameters that exemplifies the reduced efficiency of the petcoke-IGCC plant are the cold gas efficiency and heat rate. Due to the high carbon density and the reduced volatile matter of petcoke, its conversion to syngas shown by the cold gas efficiency is 9% points lower than that of coal. Similarly, the heat rate (HR) which quantifies the amount of fuel per MWh of electricity confirms the energy loss in the petcoke system as it showed to be 10% higher for the petcoke process compared to coal system.

The economic performance of the petcoke-IGCC plant is evaluated using the LCOE which is compared against the coal system as shown in tab. 4. In this study, we assumed the petcoke price to be free which is consistent with the assumption of NETL (Kramer 2003). Compared to the coal plant, this offset a huge portion of the investment cost for the petcoke-IGCC plant. Hence, the LCOE of the petcoke-IGCC plant was estimated as 123.51 $/MWh which is 12% lower than that of coal-IGCC plant. But for an NGCC plant of the same capacity and efficiency of 42.4% HHV, an LCOE of 87.6 $/MWh was estimated (Adams II, Hoseinzade et al. 2017). However, it should be noted that the petcoke-IGCC is presented as a disposal strategy and not to compete economically with such standard power plants.

A quick CO_2 emission comparison of the proposed petcoke-IGCC plant to that of coal showed a 24% reduction in GHG emissions due to the high emission of the coal upstream process. However, to better understand the effect of the proposed design, its CTG life cycle emission is compared to the commercial SCPC process that it could displace.

Life cycle impact assessment

Figure 2 shows the CTG environmental impact categories of the petcoke-IGCC and coal-IGCC plants relative to the coal SCPC plant. The ODP of the petcoke plant is 25% lower than that of coal-SCPC which is because petcoke used in this study does not contain chlorine compared compared to coal which produces more chlorinated substances during combustion operation. The life cycle GHG emissions of the petcoke process is 43% lower than the traditional SCPC which is mainly attributed to SCPC's larger upstream emissions compared to the petcoke supply chain (from a waste).

Another significant observation in the study of the life cycle of both processes is in the extent of reduction in fossil energy usage. Petcoke is considered a dirty waste product but with an inherent advantage of serving as a fuel. Hence, petcoke-IGCC has 45% lower FFD compared to SCPC, largely because petcoke is classified as a waste rather than a fossil fuel. This implies that petcoke-IGCC can displace coal-based power plants and result in both a lower net fossil fuel depletion rate and simultaneously help dispose of the petcoke. The AP of petcoke-IGCC is only about 17% lower than SCPC plant, since its sulfur emissions are still significant. The ETP for petcoke-IGCC (which assesses ecosystem toxicity potential) was 55% lower than that of SCPC.

The only impact category in which petcoke-IGCC is worse than the coal designs is the RE. This is not surprising as petcoke has a high tendency of emitting particulates that affects the human respiratory system. Other impacts such as SF, EP, CP, and NCP are also lower than the corresponding impacts for the coal plants and for brevity were not further discussed.

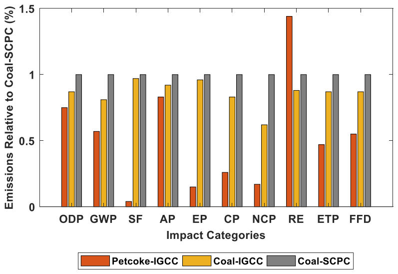

Figure 2. CTG life cycle impact categories of petcoke-IGCC and coal-IGCC relative to coal-SCPC, all with CCS

Sensitivity Analysis

Although the price of petcoke was assumed to be free, its impact on the overall economics of the process was evaluated by performing a sensitivity analysis on its effects on LCOE which characteristics the profitability of the proposed power plant. It can be seen from figure 3 that the petcoke-IGCC plant is competitive with the coal-based plant even at petcoke prices as high as 70 $/tonne (which is termed the long-term price). This price illustrates a scenario where petcoke is of high demand and given location constraints, the price roughly equals that of bituminous coal on an equivalent energy basis. However, at the feasible price of green petcoke (generally discounted to coal) results in an LCOE between 130 and 134 $/MWh which is reasonable for low-carbon electricity generation process.

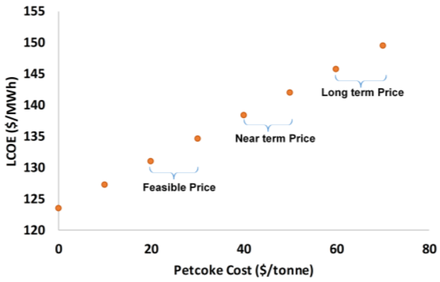

Figure 3. Effects of petcoke price on LCOE

Conclusions

This work explored the performance of a dedicated petcoke-IGCC power plant operating with CCS in terms of its technical, economic, and life cycle assessment. To better understand the performance of the petcoke-IGCC power plant, techno-economic and life cycle analyses were performed and compared to coal-IGCC and SCPC plants operating with CCS.

The results showed that petcoke-IGCC is a viable pathway for the disposal petcoke. By integrating CCS, the net lifecycle CO_2 emissions per unit of energy produced from petcoke is lower than that of either coal-IGCC or SCPC. Similarly, the estimated LCOE for petcoke-IGCC was also lower than both coal-IGCC and SCPC when petcoke was assumed to be free. The sensitivity analysis showed that petcoke-IGCC is still cost-competitive with the other plants as long as the petcoke is price is below about $30/tonne.

As this current work presents the first research article to study the comprehensive life cycle of petcoke to electricity process, it addresses the initial step of exploring the problem caused by stockpiling petcoke. In our further work, we will compare this to the life cycle environmental impacts of stockpiling petcoke in a terrestrial location such as in Alberta Canada. Also to be explored in future work is the synergy of design configurations which can combine natural gas and petcoke together into a single power plant. Effectively, the overall goal is to achieve a power plant that can serve as a viable and cost-effective means by which petcoke is safely disposed, while simultaneously reducing life cycle GHG emissions by displacing both stockpiling and either the consumption of grid electricity or the construction of new fossil-based power plants. This is especially relevant for the province of Alberta, Canada, which both produces large amounts of petcoke sent to stockpile and possesses an electric grid with a large GHG intensity.

Acknowledgments

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Chapter 5

Application of petroleum coke disposal to electricity generation: design and economics of petrolum coke oxy-combustion.

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Advanced Petroleum Coke Oxy-Combustion Power Generation with Carbon Capture and Sequestration: Part I – Design and Techno-Economic Analysis

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Abstract

This study presents a first-of-its-kind design and economic analysis of a petroleum coke oxy-combustion electric power generation technology operated with and without carbon capture and sequestration. In this work, we examined three petroleum coke oxy-combustion designs: petcoke oxy-combustion; petcoke oxy-combustion operated with carbon capture and sequestration (CCS); and petcoke oxy-combustion with CO_2 purification by distillation and CCS. The technical and economic performance of the designs were assessed based on thermal efficiency, CO_2 capture rate, pipeline CO_2 purity, CO_2 emissions, and levelized costs of electricity (LCOE). The results of our assessments yielded a base case LCOE of $84.24/MWh for the petcoke oxy-combustion design, $90.94/MWh for the petcoke oxy-combustion design operated with CCS, and $102.8/MWh for petcoke oxy-combustion with CO_2 purification by distillation and CCS. Although the design that employed CO_2 purification had higher LCOE than the other designs, its captured CO_2 stream meets pipeline standards. Therefore, this design was selected for the proposed petroleum coke oxy-combustion technology. Further analysis carried out includes the cradle-to-customer gate life cycle environmental impact assessment of the petcoke oxy-combustion power plant which is presented in Part II of this work. Thus, this work represents the first study to present the eco-technoeconomic and life cycle analysis that considered the impacts of O_2 removal from CO_2 captured from oxy-combustion exhaust via cryogenic distillation for solid fuels in general.

Keywords: Petcoke, Oxy-combustion, Electricity, CO_2 capture, GHG emission, eco-Techno-economic Analysis

1.0 Introduction

The processing of heavy oil and bitumen reserves, as well as the more desirable lighter crude oil, makes the production of petroleum coke inevitable. Petroleum coke (petcoke) is a solid waste that is generated by the processing of petroleum residues in coking units, which are common to many crude oil refinery operations [1]. As a byproduct of oil refining, petcoke is abundant. Indeed, in 2011, US refineries and Canadian upgraders produced upwards of 56 and 9 million metric tons of petcoke, respectively [2], with the high amounts of US-produced petcoke being attributable to the large amounts of Canadian oil processed in US refineries. Moreover, petcoke production shows no signs of slowing. Based on Canada's proven bitumen reserves and a petcoke yield of 15%, it is estimated that up to 5 billion tons of petcoke will be produced [2]. The increased amount of produced petcoke, coupled with limited storage capacity, has led to the stockpiling of up to 100 million metric tons of petcoke [3], which has given rise to various environmental concerns and land use challenges over time [1].

Advanced oxy-combustion technologies can offer a potentially attractive alternative to stockpiling, as they can utilize petcoke for electricity generation. In oxy-combustion, fuels are burned in the presence of high-purity oxygen (95% - 99.9%) to produce high-temperature flames with nitrogen-deficient flue gas, which enables carbon dioxide to be easily separated [4]. Although oxy-combustion has traditionally been employed in metal cutting and welding operations, researchers have recently begun to explore its potential for electricity production. For example, the capital intensive nature of current carbon capture technologies has led the US department of energy (DOE)/ National Energy Technology Laboratory (NETL) to direct research towards other technologies, such as oxy-combustion CO_2 capture, that can be retrofitted to existing coal power plants [5].

Over the years, researchers have tended to focus solely on the use of coal oxy-combustion for power generation. For instance, Kakaras et al.[6] study of a coal oxy-combustion power plant with 239 MW net output showed an efficiency of 32.3% HHV, a LCOE of €57.5/MWh, and life cycle CO_2 emissions of 0.231 tCO_2e/MWh for a 90% CO_2 capture rate. Similarly, the results of Huang et al.[7] coal oxy-combustion study of a 670 MW plant with a 94% CO_2 capture rate showed thermal efficiency, LCOE, CCA, and life cycle CO_2 emission values of 34.72% HHV, \$88.1/MWh, \$8.6/tCO_2e, and 0.136 tCO_2e/MWh, respectively. In addition, Porter et al.[8] studied a coal oxy-combustion power plant with 100% CO_2 capture; their findings showed life cycle CO_2 emissions of 0.091 tCO_2e/MWh and corresponding plant efficiency and LCOE values of 29.5% HHV and $160.7/MWh, respectively. Nevertheless, the sequestered CO_2 streams in these studies contained up to 3% oxygen, which has the tendency to corrode the transportation pipeline. Our review of the literature revealed only a limited number of studies that have attempted to further purify the CO_2 in order to remove the oxygen[9]. For example, Porter et al.[8] incorporated a distillation operation into their oxy-combustion power plant study to separate the non-condensable gases from the CO_2 stream in order to meet the pipeline specification. By adding this distillation process, Porter et al.[8] were able to achieve an efficiency of 29% HHV and an LCOE of $168.4/MWh. Recently, the NETL conducted a coal-based oxy-combustion study wherein a traditional cryogenic air separation unit was used to provide the required oxygen in the basecase design, and an advanced oxygen membrane was used to generate oxygen in 6 other cases. The results of this study showed that all 6 cases using the oxygen membrane outperformed the basecase[10]. While several studies are focusing on coal oxy-combustion power plant analysis, to the knowledge of the authors, little or no attention has been given to petcoke oxy-combustion.

Although some studies have shown the technical and economic feasibility of converting petcoke to fuels, chemicals, and electricity[11-14], they have predominantly focused on the gasification pathway, which employs a highly energy-intensive solvent-based technology to capture CO_2. In contrast to this approach, oxy-combustion conversion technology takes advantage of the flue gas containing primarily CO_2 and H_2O, which requires relatively little energy to separate[15]. Thus, this work focuses on exploring the design, economics, and life cycle environmental performance of the petcoke oxy-combustion process. While the design and economics are presented in this paper, the life cycle environmental impact assessment is presented in Part II of this paper[16]. Three petcoke oxy-combustion processes were designed and examined: petcoke oxy-combustion (POXY); petcoke oxy-combustion with CCS (POXY CCS); and petcoke oxy-combustion with CO_2 purification by distillation and CCS (POXYD). The POXY design showcases the system's performance of a status quo process operated without CCS while the POXY CCS design highlights the benefits and parasitic electrical demand of adopting CCS. Finally, the POXYD design further presents the overall performance of the petcoke oxy-combustion system as it fits into the existing CO_2 pipeline. In part I of this work, these designs were compared in terms of their technical performance and economic feasibility, both to each other and to that of status quo coal-fueled power plants that employ SCPC, IGCC, and oxy-combustion technologies [9]. Furthermore, a comparison of these plants' performances enabled us to draw conclusions about the most efficient means of petcoke disposal, which we have proposed in previous studies [14; 17].

Figure 1 shows the process flow diagrams of the proposed petcoke oxy-combustion power plants, which differ in terms of how CO_2 is captured and purified. The upstream portions of the plant are the same for all three processes, which is described next.

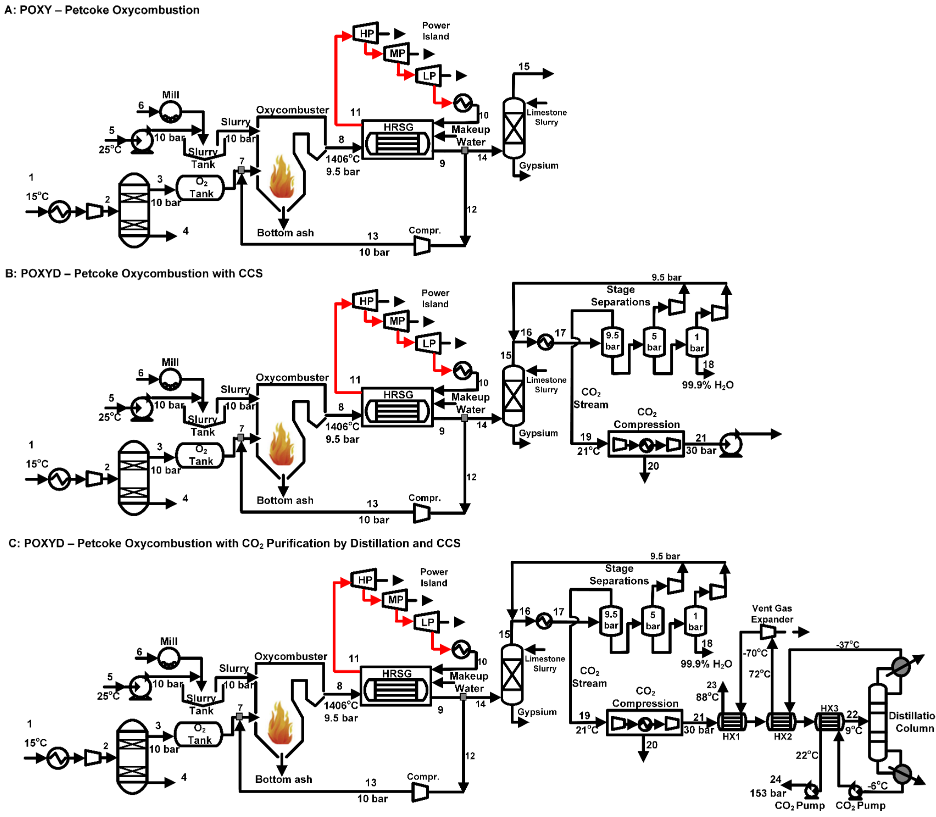

Figure 1: Process flow diagrams of petcoke oxy-combustion technology operated with and without CCS, for three process variants. (A) POXY; (B) POXY CCS; (C) POXYD.

First, the stockpiled petcoke is crushed, mixed with water to form slurry, and fed to the oxy-combustor with 98 mol% pure oxygen at a stoichiometric ratio, or just slightly above it. Next, combustion takes place, producing hot flue gas predominantly consisting of carbon dioxide and steam with small amounts of O_2, N_2, Ar, SO_2, and SO_3. The produced flue gas is then sent through the heat-recovery steam generator (HRSG) to produce steam at subcritical and supercritical conditions. Due to the high temperature of the oxy-combustion process, some portion of the flue gas is recycled into the combustor, which helps to control its temperature through dilution. The produced steam is then sent through a high-pressure turbine (HPT), an intermediate pressure turbine (IPT), and a low-pressure turbine (LPT), respectively, to produce electricity. The remaining unrecycled flue gas is sent to the flue gas desulfurization (FGD) unit where sulfide impurities are removed with the aid of limestone, producing gypsum in the process. Notably, a de-NOx step is not required, as there is only a small amount of nitrogen in the system and so NOx formation is minute. At this point, the processes differ depending on the case. For the POXY case (Figure 1A), the flue gas leaving the FGD is simply vented to the atmosphere, having been desulphurized. In the POXY CCS (Figure 1B) and POXYD (Figure 1C) designs, the flue gas leaving the FGD unit is sent to a three-stage flash drum sequence, where it is separated into CO_2 and H_2O rich streams. In the POXY CCS Case (Figure 1B), the CO_2 stream recovered from the three stage flash sequence is compressed to supercritical conditions and then pumped to 153 bar for transport to the CO_2 sequestration site. However, the CO_2 stream contains up to 3% O_2 at the plant exit gate, which is undesirable as it tends to corrode the CO_2 pipeline [18], and is above the O_2 tolerance limits of most known CO_2 transportation pipeline [19]. Nevertheless, this O_2 is allowed to remain in the captured CO_2 of the POXY CCS case (Figure 1C) so that it can be readily compared with the rest of the literature because almost all comparable studies that the authors could find (coal-based oxy-combustion with CCS) consider captured CO_2 under similar conditions [9]. The POXYD case (Figure 1C) goes a step further and includes a cryogenic CO_2 purification process to remove the O_2 present in the CO_2 stream before compression for pipeline transport.

The key novelties of the paper are not only that this is the first design and eco-techno-economic analysis (eTEA) of a petcoke-based oxy-combustion process, but that this is the first paper to consider the impacts of O_2 removal from CO_2 captured from oxy-combustion exhaust via cryogenic distillation for solid fuels in general. In this work, we present the three process designs, their simulation results, and a comparative eTEA, with the first complete life cycle analysis of the proposed processes presented in Part II of this work [16].

2.0 Methodology

2.1 Process model physical properties and assumptions

In this study, we used delayed petcoke as the feed with a net power output of 550 MWe. This size of the plant was chosen to be consistent with our recent petcoke integrated gasification combined cycle (IGCC) study [17] and to enable easy comparison with the power plants presented in our prior review study [9]. Table 1 shows the properties of the Suncor delayed coke used in this work.

Table 1: Properties of delayed coke [20].

Delayed coke			
HHV (MJ/kg)	34.7		
Ultimate analysis (wt. % dry)			
C	84.9	Cl	0
H	3.9	Ash	3.1
N	1.3	O (diff)	0.8
S	6		
Proximate analysis (wt. %)			
Moisture	1.8	Fixed carbon	83.3
Volatile matter	11.9	Ash	3

Aspen Plus v10[21] was the process simulation tool used to model the entire petcoke oxy-combustion power plant. In addition, a number of different physical property models were also employed due to the complexity of individual sub-processes in the oxy-combustion process. As in our previous studies, we widely employed the Peng-Robinson with the Boston-Mathias alpha function (PR-BM) in the flowsheet [22]. In addition, we used the Predictive Redlich-Soave (PSRK) model for the CO_2-H_2O separation, capture, and compression of CO_2 as it has shown to perform accurately at very high operational pressures [19]. The reader is referred to those studies for explanations of why those models were chosen. Finally, the STEAMNBS package was used to model the Rankine cycle. The thermophysical properties of the chemical species considered in the simulations used the Aspen Plus APV100 Pure-36 databases for the conventional components. The non-conventional substance, petcoke, was specified as a pseudo-component using the properties listed in Table 1. The stream conditions for each of the proposed designs are presented in Appendix Tables A1-A3 with the stream numbers for each design corresponding with the numbers in Figure 1.

Table 2: Operating parameters and assumptions.

Main design parameters		
Unit	**Parameters**	**Ref**
ASU	Oxygen purity (>98%) @ 32°C, P = 10 bar	[19]
Oxy-Combustor	Slurry water/ petcoke (35w%/65w%) Stoichiometric condition with flue gas recycle	[23]
CO_2 Compression	Multistage compressor with intercoolers CO_2 Purity (>95%) P = 153 bar	[19]
Cooling Tower	Wet bulb temp: 11 °C; Approach temp: 5°C; Cooling water range 11°C	[24]
Assumptions		**Ref**
Min temperature approach in heat exchangers	10°C	
Supercritical steam	602°C / 250 bar	[25]
Subcritical steam	620°C / 50 bar /10 bar	[23; 25]
Isentropic efficiency in compressors	80%	[19]
Mechanical efficiency in compressors	100%	[19]
Max pressure ratio in compressors	5	[19]
Pump efficiency	80%	[19]

2.2 Model process descriptions:

2.2.1 Air separation unit

Unlike SCPC power plants, oxy-combustion technology requires the use of high-purity oxygen. Commercial oxygen production for oxy-combustion is typically done via the cryogenic process, which entails the compression, cooling, liquefaction, and distillation of air in an air separation unit (ASU). In this paper, we adopted the ASU separation coefficients detailed in [24] and implemented them in Aspen Plus using SEP and calculator blocks to compute the mass balances that result from the production of 98% pure oxygen with a parasitic load of 1 MW/t/hr [24]. Thus, the unit was fully considered when computing all costs, flows, and emissions impacts in the analysis.

2.2.2 Oxy-combustion

The oxy-combustor employed in this study was based on a commercial air-fired pulverized bituminous coal combustor [10] operated at 10 bar. The delayed coke is crushed, mixed with water according to the proportions shown in Table 2, and sent to the combustor. Oxygen is fed into the combustor at the stoichiometric ratio, which if not diluted can cause flame temperatures to exceed 3800°C; however, the temperature is controlled at about 1400°C with the aid of the recycled flue gas. Heat loss to the environment during combustion was assumed to be 2% of $\mathrm{HHV}_{\mathrm{petcoke}}$ which was considered for the combustor energy balance. To enhance the atomization of the petcoke slurry particles, steam from the HPT is injected into the combustor [23]. We followed the recommendation of Hong et al. [23] such that the amount of steam injected into the combustor was approximately 10% of the petcoke feed rate. Finally, the hot flue gas exiting the combustor was sent to the HRSG where it was used to generate supercritical and subcritical steam.

2.2.3 HRSG and power generation

The heat from the flue gas exiting the combustor is recovered to produce the steam that is required at the power island. In the HRSG section, superheaters, once-through boiler, and an economizer were used to produce steam which is sent to the power island that employs a series of turbines, feedwater reheaters (FWR), and a deaerator for power generation as shown in Figure 2. The feedwater pump is used to raise the BFW to the deaerator pressure of 10 bar before the second feedwater pump raises it to a supercritical pressure of 250 bar. The steam at supercritical condition passes through the FWR where it is heated regeneratively before entering the HRSG where it is further heated to 605°C at 250 bar [25]. The supercritical steam is then sent to the HPT where it is expanded to 50 bar, producing electricity via the Rankine cycle. As noted in the previous section, an amount of steam corresponding to 10% of the mass flow rate of petcoke is recycled into the combustor upon exiting the HPT [23]. The flow rate of this steam sent to the combustor is equal to the feedwater makeup. The reheat stream from the HPT is reheated to subcritical conditions at the HRSG, reaching a temperature of 620°C [23; 25]. The subcritical steam at 50 bar is then sent to the IPT where it is expanded to 10 bar, which produces additional electricity. Upon exiting the IPT, a portion is sent back through the FWRs, while the reheat stream is again reheated to subcritical condition at the HRSG to 620°C [23]. Finally, the subcritical steam at 10 bar is expanded to below atmospheric pressure at the LPT, which produces more electricity. The steam exiting the LPT is sent to the cooling tower where it is condensed at 33°C and pumped through the deaerator before being raised to supercritical condition.

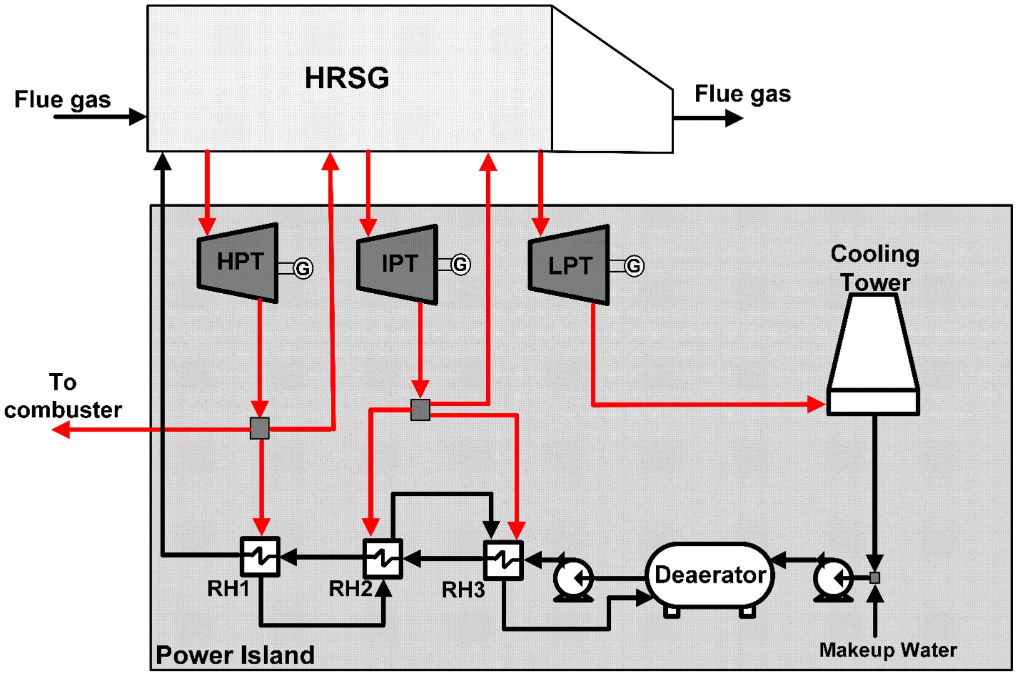

Figure 2: HRSG and power island design.

2.2.4 Flue gas desulfurization

Flue gas exiting the HRSG is sent to the FGD unit where impurities such as SO_2 and SO_3 are selectively removed by reacting it with limestone. This takes place in the contacting tower at temperatures between 150 and 370°C [26] operated at about 10 bar which is higher than the conventional atmospheric FGD. Due to the limestone slurry that was used, we employed the wet scrubber system, which involves sending the flue gas in through the bottom of the tower and the slurry in through the top. This approach causes the flue gas to become saturated by the evaporated water vapor from the slurry, which enhances the dissolution of sulfur oxides and reacts with slurry limestone as shown by the following series of reactions [27].

$$CaCO_3 \leftrightarrows CaO(s) + CO_2(g) \tag{1}$$

$$CaO(s) + SO_2(g) + \frac{1}{2}O_2(g) \leftrightarrows CaSO_4(s) \tag{2}$$

$$CaO(s) + SO_3(g) \leftrightarrows CaSO_4(s) \tag{3}$$

While the reacted sulfur oxides fall to the bottom of the scrubber as solid gypsum, the treated flue gas exits through a mist eliminator. Due to the complexity of the FGD model, we assumed that the FGD reaction follows eqns. 1-3, and we estimated the energy consumption to be 1.6 MW/kg of flue gas [10].

2.2.5 CO_2/H_2O separation and compression (POXY CCS and POXYD cases only)

Unlike the air-fired system, oxy-combustion technology relies on flash separating the CO_2 and H_2O in the flue gas—which is low cost and requires relatively little energy—in order to produce high purity CO_2 ready for pipeline transport and sequestration. In the other two cases, the flue gas leaving the FGD unit is sent to a three-stage flash cascade at decreasing pressure levels, where it is separated into CO_2 and H_2O rich streams. Although a single flash drum could be used at high pressure to condense out the water from the flue gas, too much CO_2 is dissolved in the liquid water product, reducing CO_2 capture rates. The secondary and tertiary flash drums at lower pressure levels allow for nearly 100% capture of CO_2 since the solubility of CO_2 in water at atmospheric pressure is low. However, the majority of CO_2 is still captured at high pressure, meaning that the parasitic load of the recycle compressors for the second and third stage vapor products is low. The result is a system that captures essentially 100% of the carbon with a relatively small parasitic load, with a nearly pure water product. The design for this step used in this work was based on a similar approach used in solid oxide fuel cell power plants with CO_2 capture which have a similar flue gas composition [19], except adapted to petcoke oxy-combustion conditions, such as the O_2 concentration. The flue gas exiting the FGD is cooled to 21°C before being sent through the three-stage flash system proposed by Adams et al. [15] to produce a CO_2 stream which is 95% pure. A multistage compressor with an intercooler is then used to compress the CO_2 stream to supercritical conditions before pumping it to 153 bar, which is typical of sequestration pipeline conditions. The water produced during the 1st flash separation stage is passed through the 5 bar and 1 bar flash drums, which are each equipped with a recycling compressor at the vapor outlet. The produced water is over 99.9 mol% pure and can be reused in the system to offset overall water consumption.

2.2.6 CO_2 purification (POXYD case only)

As mentioned earlier, the oxygen content in the captured CO_2 stream exceeds the permissible limit, which means that the CO_2 stream can potentially cause pipeline corrosion. Therefore, for the POXYD case, a cryogenic CO_2 purification process is employed to remove the O_2 present in the CO_2 stream. This process uses a distillation column for O_2/CO_2 separation with a collection of integrated heat exchangers to minimize refrigeration duty requirements. The design of the column allows some of the captured CO_2 to exit with the O_2 since O_2 purity is not a priority. Although this reduces carbon capture rates to around 95%, costs and refrigeration duties are more feasible than if CO_2 capture rates close to 100% are required. The high purity CO_2 stream is pumped to 153 bar and transported to the sequestration location, while the distillate is vented to the atmosphere and is the primary source of direct CO_2 emissions from the process, albeit a relatively small amount. Since the CO_2 stream oxygen concentration in this study was about 3%, cryogenic purification was employed to reduce it to less than 10 ppm. The cryogenic purification system designed for this study is shown in Figure 3.

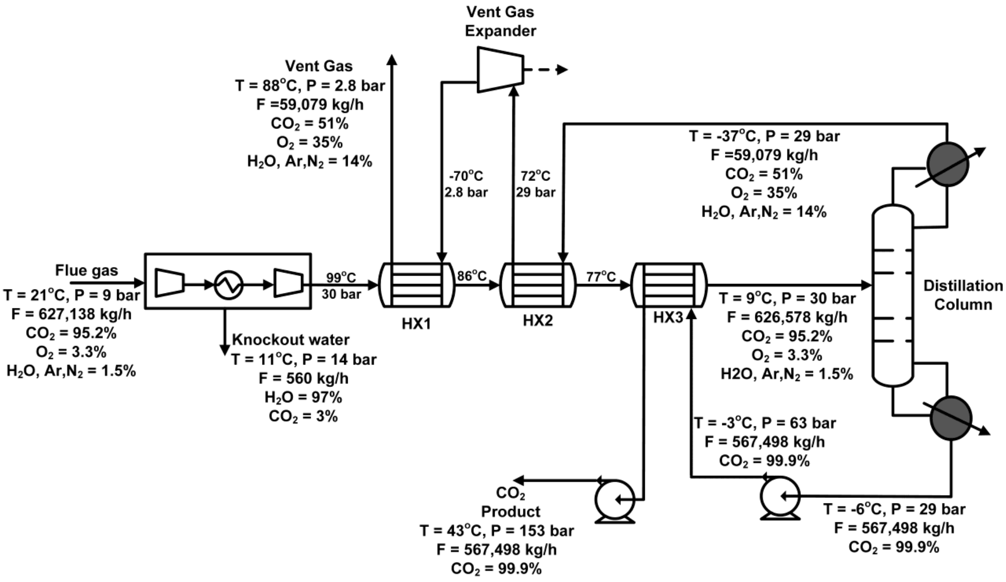

Figure 3: Process flow diagram of CO_2 purification design. Adopted from [10].

The flue gas exits the three-stage flash separation system at about 9 bar and is then compressed to 30 bar. It is then sent through the heat exchangers to achieve a temperature of approximately 9°C before entering the feed stage of the distillation column. Since the desired target for the bottom stream is known (less than 10 ppm of O_2), the top product specification is a design choice. In this study, we were able to achieve an inlet CO_2 mass recovery of 95% and a mass fraction of 10 ppm by varying the reflux ratio and the boil-up ratio, respectively. The top product is expanded[1] to produce power before being vented as gas, while the bottoms product is pumped to supercritical condition and subsequently to 153 bar.

While the excess heat from the process is sufficient for satisfying the reboiler duty, the condenser duty is provided by the propane refrigeration cycle that was modeled in this work and is shown in Figure 4. The propane refrigeration cycle was designed using the optimal design parameters detailed in [28]. The refrigerant was cooled by creating a pressure drop across the valve based on the Joule-Thompson effect. In this design, the outlet of the value was set to 1 bar, which resulted in a propane temperature of -43°C. The coolant was then sent across the condenser of the CO_2 stream distillation column to provide the required cooling duty. Exiting the condenser, it was compressed to 14 bar to maintain the pressure of the working fluids. Finally, the vaporized propane was condensed and the loop was maintained. Using the corresponding Aspen Plus model, we found that this cycle could provide 48.6 MW of cooling at -43°C per 1 kg/hr of propane coolant flow and required 32.3 MW of compressor work and 776.9 kW of cooling tower load using cooling water at 30°C.

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[1] The extent of the gas expansion was chosen such that dry ice formation is avoided

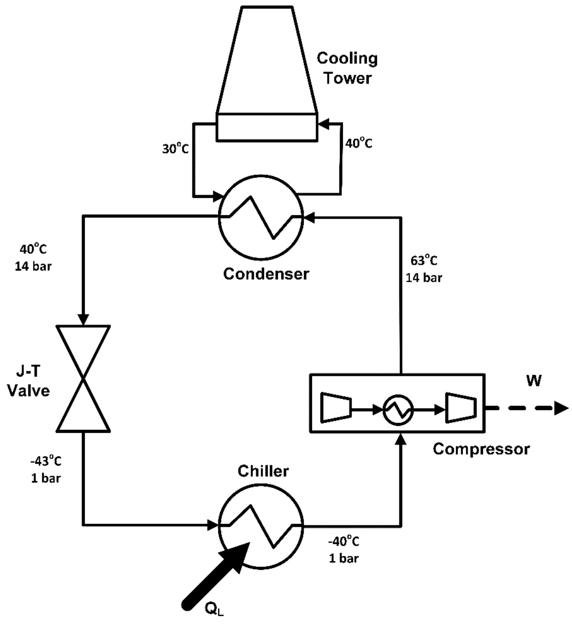

Figure 4: Propane refrigeration cycle.

2.2.7 Heat integration (utilities and cooling water)

In this study, the heat requirements of the plant were provided by process-to-process heat exchange based on heat exchanger network (HEN) design carried out with Aspen Energy Analyzer (details of the HEN can be found in the supporting document). The HEN provided for all process heating needs by utilizing waste heat, but a cooling tower was required for the propane refrigeration cycle and other aspects of the plant. Thus, the design of the cooling tower is presented. In this design, we employed a mechanical draft evaporative cooling tower system with a temperature approach of 5°C and a cooling range of 11°C [24]. To account for the cooling tower makeup, values of 5%, 0.8%, and 2% were used for losses resulting from evaporation, cycles of concentration, and evaporative and drift losses, respectively, based on Edgar et al. [29]. The parasitic electrical consumption of the cooling tower pump and fan were calculated using the correlation reported by Turton et al. [30] using a pump efficiency of 80% and a pressure drop of 1 bar.

2.3 Cost analysis

In order to evaluate each plant's profitability, a techno-economic analysis of the designs was conducted using the cost estimation assumptions given in Table 3. Equipment sizes and costs were estimated using Aspen Plus mass and energy balance. Equipment costs were estimated based on the NETL oxy-combustion study [10], with the sixth-tenths rule being used to scaleup the size of each unit's operations. Each plant's variable operating costs, which consisted of consumables such as petcoke feed rate, limestone, and feed water, were obtained from literature, while labor, maintenance, and overhead costs were estimated using the methods given by Seider et al. and Peters et al. (Table 4). All of the equipment costs were scaled, and the variable costs were inflated (using inflation rate) to US$2016 in order to ensure consistency with our meta-study cost year [9]. Finally, the discounted cash flow rate of return (DCFROR) was used to calculate the LCOE for each design by iterating the annual net income to obtain a net present value of zero.

Table 3: Cost estimation parameter assumptions.

Parameter	Value	Ref
Construction period (yrs)	2.5	
Plant loan (yrs)	30	
Plant loan interest	9.50%	[31]
Debit/Equity (%)	50/50	[32]
Inflation rate (%)	2.79%	[31]
Tax Rate	40%	[31]
Equity Rate of Return	12%	[13]
Depreciation Method	MACRS	
Working capital	15% TPC	[33]
Length of start-up (yrs)	0.25	
Operating Time (hrs)	8000	

Table 4: Fixed and variable operating costs estimations.

Fixed costs (Labor, Maintenance, and Overheads)		**Ref**
Direct wages and benefits (DW&B)	32 operators/shift	[34]
Direct salaries and benefits	15% of DW&B	[34]
Operating supplies and services	6% of DW&B	[34]
Tech. assistance to manufacturing	$60,000 base for 5 shifts	[34]
Control laboratory	$65,000 base for 5 shifts	[34]
Wages and benefits (MW&B)	173% of Labor cost	[10]

Salaries and benefits	25% of MW&B	[34]
Materials and services	100% of MW&B	[34]
Maintenance overhead	25% of MW&B	[34]
Operating Overhead	22.8% of M&O-SW&B	[34]
Property Insur. & Tax	1% of FCI	[33]
Feedstock, product, and byproducts prices		
Petcoke (Feedcost)	0.0 $/tonne	[13]
Utility		
Boiler Feed Water	$0.5/tonne	[34]
Solvents, Catalysts & Wastes		
Wastewater Treatment	$0.6/tonne	[33]
Ash	$14.1/tonne	[24]
Limestone	$31.8/tonne	[10]
CO_2 transportation and storage cost	$11/tonne	[10]
CO_2 Emission Tax (to direct plant emissions)	$50/tonne	[31]

3.0 Results

3.1 Systems performance

Table 5 summarizes the overall system performance of each petcoke oxy-combustion design, including the plant feed sizes, gross and net power outputs, design efficiencies, heat rates, and CO_2 sequestration rates and emissions.

Table 5: Summary of petcoke oxy-combustion designs system performance.

	Unit	POXY	POXY CCS	POXYD
CCS Enabled		No	Yes	Yes
Petcoke feed rate	tonne/h	178	183	193
Petcoke feed capacity	MW_{HHV}	1715	1769	1863
Total power generated	MW	711	733	772
Total parasitic load	MW	161	183	221
Net power output	MW	550	550	550
Net thermal efficiency	HHV%	32.1	31.1	29.5
Heat rate	MJ_{HHV}/MWh	11,225	11,577	12,196
CO_2 sequestered	tonne/h	0	596	567
Cradle-to-gate CO_2 emission	$kgCO_2$/MWh	999.3	0.46	54.7
Cradle-to-gate life cycle GHG emission	$kgCO_2$eq/MWh	999.5	0.63	54.9

The petcoke feed rate for the POXY design is 0.32 tonnes per MWh of electricity; in contrast, the POXY CCS and POXYD designs require the consumption of 3.1% and 8.5% more petcoke, respectively. In terms of energy, the feed capacity for 550 MW of net power requires inputs of 1715, 1769, and 1863 MW_{HHV} petcoke for the POXY, POXY CCS, and POXYD designs respectively, which is typical for most commercial power plants with such capacity [10; 35]. This is further shown in the heat rate of the designs, with the POXY plant consuming 11,225 MJ_{HHV} of petcoke per MWh of net electricity produced. With respect to parasitic load, which represents the system's total electrical demands, the POXY CCS and POXYD designs required 13.8% and 37.6% more electricity, respectively, compared to the POXY plant. It is evident that the reduced parasitic load of the POXY plant is due to the relatively low amount of petcoke feed required to achieve the same net electricity output. Table 6 shows the breakdown of the total parasitic load by sections in the plant for each design.

Table 6: Summary of petcoke oxy-combustion designs parasitic load (in MW of electricity).

	POXY	POXY CCS	POXYD
CCS Enabled	No	Yes	Yes
Coal handling and Preparation	2.91	3.01	3.17
Ash Handling	1.02	1.05	1.11
Flue Gas Recycle Compressor	11.5	11.9	12.5
Air Separation Unit	136	140	148
FGD Pumps and Agitators	1.30	1.34	1.41
Cooling Tower Fans	8.27	8.53	9.77
CO_2 Separation	0	0.07	0.08
CO_2 Compression	0	17.1	0
CO_2 Purification & Pumping	0	0	45.7
Total Load	161	183	221
Total Power Generation	711	733	772
Net Power Output	550	550	550

As expected, the ASU consumes the highest amount of electricity, accounting for 84%, 77%, and 67% of the total parasitic loads for the POXY, POXY CCS, and POXYD designs, respectively. However, the section of the CCS-enabled designs responsible for CO_2 compression and purification also requires a large amount of electricity. Fortunately, one key advantage of oxy-combustion technology is the low parasitic load of CO_2 separation, which corresponds to a maximum of 1.38 x 10^{-4} MW per MWh of net electricity. By comparison, the solvent-based capture method employed in the SCPC and IGCC power plants consumes 3.02 x 10^{-2} [35] and 2.3 x 10^{-2} [19] MW per MWh net electricity, respectively.

3.2 CO_2 capture

The overall goal of this research was to demonstrate oxy-combustion technology's ability to reduce GHG emissions, which is largely due to the relative ease with which it enables CO_2 capture. As shown in Figure 5, the POXY design performs poorly in terms of GHG emission reduction, emitting 999 kgCO_2eq/MWh. This output is similar to the SCPC design without CCS, which produces 944 kgCO_2eq/MWh [35]. In contrast, the POXY CCS design provided a CO_2 capture rate of nearly 100%, with cradle-to-product GHG emissions as low as 0.63 kgCO_2eq/MWh. This dramatic decrease in GHG emissions is made possible due to the design's use of multi-stage flash separation to separate CO_2 and water from the flue gas, and, due to the use of a waste product as the primary energy source to which no CO_2 emissions are attributed for its production. However, like almost all coal-based oxy-combustion studies, this result optimistically assumes that the captured CO_2 can be sequestered even though the oxygen concentration in the flue gas is about 3%, well above permissible limit for pipeline transportation (see Table 7). Thus, it is necessary to further purify the CO_2 stream by removing the non-condensable gases, as modeled in POXYD design. This purification model distinguishes our work from most of the oxy-combustion studies reviewed in our meta-study [9], as most of the authors of these studies did not consider the effects of oxygen in the captured CO_2 stream. For the POXYD design, a GHG emission of 54.9 kgCO_2eq/MWh was computed, which is still an order of magnitude reduction compared to the status quo.

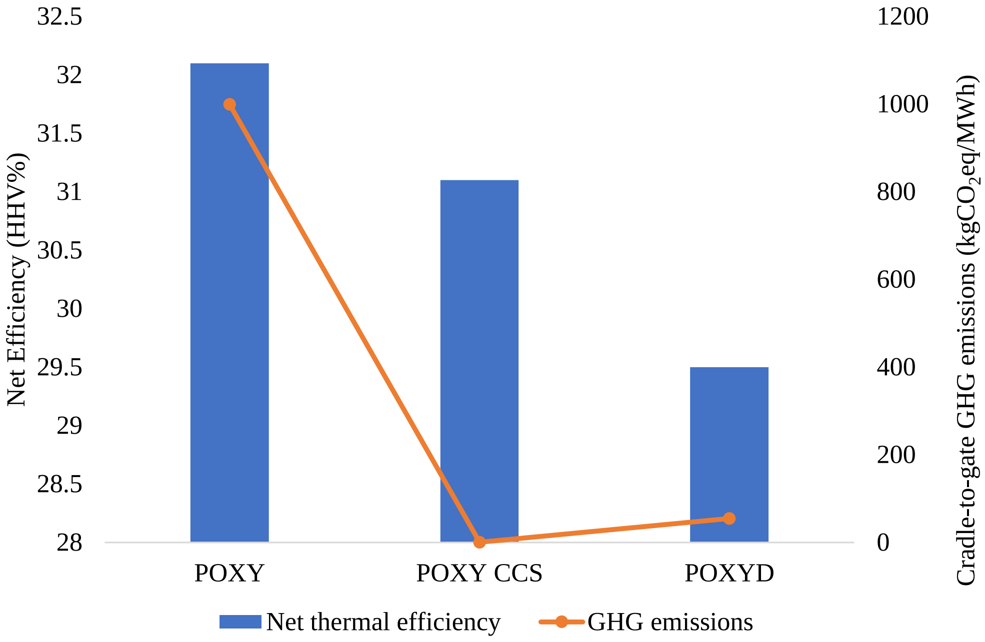

Figure 5: Net efficiency and GHG emissions of the proposed petcoke oxy-combustion designs.

As shown in Figure 5, the POXY CCS design emits 99.2% less CO_2 than the POXYD design. This disparity is due to the design of the distillation column, which allowed 5% of the inlet CO_2 to leave through the top of the column because of the higher parasitic energy demand of the condenser when 100% CO_2 is captured. The choice of capture rate is a tradeoff between energy demand and emission reductions, which creates an opportunity for further investigation via optimization. However, a detailed study of these tradeoffs was not considered in the present work. The respective concentrations of the constituent components of the CO_2 stream to be transported by pipeline to the sequestration site are listed in Table 7.

Table 7: Composition of captured CO_2 stream for sequestration via pipeline transport.

	Kinder Morgan Pipeline Specification [18]	POXY CCS	POXYD
CCS Enabled		Yes	Yes
Meets pipeline Spec?		No	Yes
H_2O	690 ppm	337 ppm	401 ppm
CO_2	>95%	95.1%	99.9

H_2S	10-200 ppm	trace	trace
CO	no specification	trace	trace
C_xH_y	<5%	trace	trace
H_2, N_2, Ar	<4%	1.34%	0.44 ppm
Oxygen	<10ppm	3.49%	9.4 ppm
NO_2	no specification	0.28 ppm	0.31 ppm
N_2O	no specification	0.01 ppm	0.01 ppm
SO_2	no specification	305 ppm	338 ppm
SO_3	no specification	0.72 ppm	0.80 ppm

3.3 Levelized cost of electricity

Cost analyses of the three petcoke oxy-combustion designs were carried out to ascertain their LCOE, which can aid in determining their respective profitability. Table 8 provides a summary of each design's equipment costs by section, total capital investment (TCI), operating expenditures (OPEX), and annual gross and net electricity generate rates. The POXYD design has a higher TCI and OPEX compared to the POXY and POXY CCS designs. This is expected given its gross annual electricity generation rate, which is 8.6% and 5.4% higher than the POXY and POXY CCS designs, respectively. This is because the analysis standardizes each design to 550 MW net output, and so a higher generation rate is needed to account for the greater parasitic loads in the POXYD case.

Table 8: Summary of petcoke oxy-combustion costs and system performance (in US$2016).

Scenario			
Design Configuration	POXY	POXY CCS	POXYD
CCS Enabled	No	Yes	Yes
Capital Cost by section(M$)			
Air separation unit	301	307	316
Petcoke handing & sorbents	34.4	35.1	36.2
Slurry prep & feed	16.0	16.3	16.8
Oxy-combustor	286	291	300
Gas cleanup & piping	114	116	120
Feedwater & miscellaneous BOP system	69.7	71.1	73.2
CO_2 removal & compression	-	11.0	140
Steam turbines & generators	143	146	150
HRSG, ducting & stack	20.3	20.7	21.3
Cooling water system	38.7	39.5	40.7
Accessory electric plant	92.5	94.3	97.3

Instrumentation & control	23.3	23.7	24.5
Improvements to site	12.3	12.5	12.9
Building & structures	50.5	51.4	53.1
Cost breakdown at 85% capacity factor			
Total capital investment (M$)	1847	1900	2157
Annual operating cost (M$/yr)	89.7	109	121
Gross electricity generated (MWh/yr)	5,687,520	5,865,301	6,179,124
Net electricity generated (MWh/yr)	4,400,000	4,400,000	4,400,000

Table 9 shows the LCOE for the three petcoke oxy-combustion designs considered in this study. Unsurprisingly, when carbon tax was omitted (to direct plant emissions only), the LCOE of the POXY design was 7.4% and 18% lower than the POXY CCS and POXYD designs, respectively, at $84.24 per MWh. Factoring in the cost of CO_2 T&S, the LCOE of the POXY CCS and POXYD designs showed increases of 15.1% and 12.8% compared to the base case (LCOE without carbon tax and without T&S cost). The POXY CCS design's comparatively greater increase in LCOE is due to its near 100% CO_2 capture rate, which results in a higher amount of CO_2 transported and, thus, higher transportation and storage costs.

Table 9: LCOE of the petcoke oxy-combustion designs.

	Unit	POXY	POXY CCS	POXYD
CCS Enabled		No	Yes	Yes
LCOE without carbon tax and without T&S cost	$/MWh	84.24	90.94	102.8
LCOE without carbon tax and with T&S cost	$/MWh	84.24	104.7	115.9
LCOE with carbon tax and without T&S cost	$/MWh	134.6	90.96	105.5
LCOE with carbon tax and with T&S cost	$/MWh	134.6	104.8	118.7

When a carbon tax of $50/tonne was applied, the POXY design became the most costly, with an LCOE of $134.6/MWh. This represents a 59.8% increase in LCOE compared to the base case. The addition of the carbon tax did not really affect the LCOE of the POXY CCS design due to its near 100% capture of CO_2, but it did cause an increase of $2.76/MWh for the POXYD design. Finally, while the addition of both the carbon tax and T&S costs did not affect the LCOE of the POXY design, it did increase the LCOEs of the POXY CCS and POXYD designs by 15.2% and 15.5% respectively compared to their base case LCOE. Nevertheless, it can be concluded that the

POXYD design’s LCOE is cost-competitive, especially in a moderate ($50/tonne) carbon tax scenario.

3.5 Sensitivity analysis

A sensitivity analysis was conducted on the parameters that were used in the economic analysis of the three petcoke oxy-combustion designs, which produced their respective LCOEs, in order to determine how these parameters affect the LCOE. Specifically, the sensitivity analysis was considered for the following parameters: rate of return (ROR) which was varied between 8% and 25%, petcoke purchase price ($0/tonne to $50/tonne), CO_2 emission tax ($0/tonne to $80/tonne), CO_2 transportation & storage (T&S) costs ($5/tonne to $15/tonne), operating hours (7200 to 8760 hrs/yr), and capacity factor (50 to 95%). While one parameter was manipulated, the others were kept constant in order to understand how the manipulated parameter impacts the LCOE. It is noteworthy to mention that the uncertainties considered were largely market uncertainties, that model parameter uncertainties were not considered. However, the sensitivity analysis is still useful because, for example, if a power plant turns out to be less efficient than was computed by the model, it means that the equivalent capital and operating costs per MWh of electricity produced would increase, and so that is reflected in the economic sensitivity analysis. Furthermore, since there are limited data on the cost of a pressurized FGD, we have varied the cost of a FGD unit designed to operate at atmospheric condition in order to ascertain its effect of the LCOE. The sensitivity analysis plots for the manipulated parameters are shown in Figures 6-12.

Figure 6 shows the results for the manipulations of the ROR and its effect on the LCOEs of the POXY, POXY CCS, and POXYD designs. As can be seen, the ROR exhibited a nonlinear relationship for each of the designs, with the POXYD design showing the highest increase in LCOE, rising to $148.9/MWh at an ROR of 20%. This is due to the high slope of the POXYD design (slope of 5.89) compared to the POXY and POXY CCS designs with slope of 5.04 and 5.19 respectively. An ROR of this size reflects a high-risk business for which power generation technology can be classified as a mature technology. Thus, it is expected that the system will operate within an ROR range of between 10% and 15%, with an ROR of 12% being used as the base case.

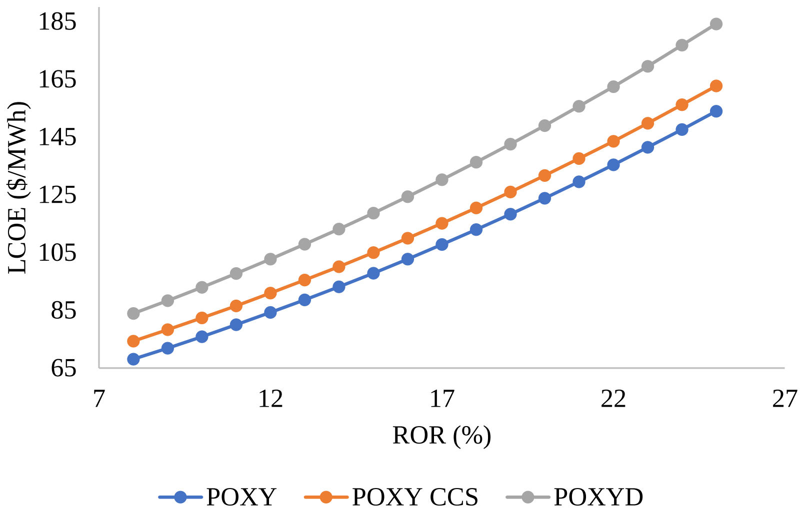

Figure 6: Sensitivity analysis of the effects of ROR on the LCOEs of the various petcoke oxy-combustion designs.

In assuming the cost of petcoke at $0/tonne, we clearly implied no feasible cost, even for transportation, which is consistent with NETL's assumption [13]. If this assumption turns out to be true, we anticipate the demand of petcoke to increase over the year, which would create some monetary value for petcoke. Thus, we varied the cost of petcoke in order the ascertain its overall impact on the LCOEs of the proposed designs. Figure 7 shows a linear relationship between the cost of petcoke and the LCOE for each of the proposed designs, which is to be expected. A slope of 0.33, 0.34, and 0.35 for the POXY, POXY CCS, and POXYD designs respectively were obtained implying a less than ¢40/MWh increase in LCOE per unit increase in price of petcoke. Assuming a petcoke cost of $25/tonne, which is approximately half the cost of US bituminous coal, the LCOEs of the POXY, POXY CCS, and POXYD designs would be $92.4/MWh, $99.3/MWh, and $111.6/MWh, respectively. Even in a worst-case scenario wherein petcoke becomes a premium power-generation fuel and rises in cost to $50/tonne, the LCOEs of POXY, POXY CCS, and POXYD were still $100.5/MWh, $107.8/MWh, and $120.5/MWh, respectively, which is still comparable to the LCOEs of the SCPC and IGCC plants.

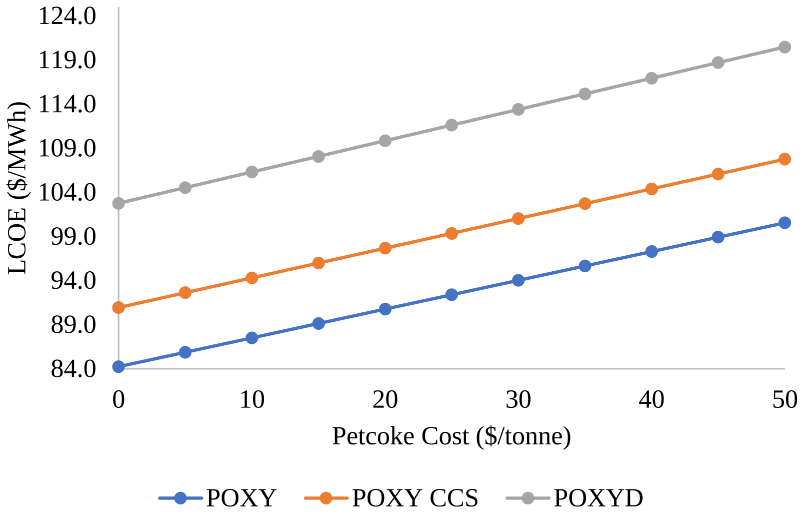

Figure 7: Sensitivity analysis of the effects of petcoke price on the LCOEs of the various petcoke oxy-combustion designs.

As mentioned earlier, the base case LCOEs were estimated without the CO_2 emission tax, which resulted in the POXY design being the most economical. However, the LCOE for this design becomes incredibly high when the carbon tax is applied. With a slope of 1.01, this implies a $1.01/MWh increase in LCOE for every $1 charged for CO_2eq emitted. As can be seen in Figure 8, the LCOE of the POXY design went up to $164.8/MWh at a CO_2 emission tax of $80/tonne. This is because of the high amount of CO_2 emitted (999.5 kgCO2eq/MWh) by the POXY design as it is operated without CCS. Even at a benchmark CO_2 emission tax of $50/tonne, the LCOE of the POXY design is $134.6/MWh which is higher than the CCS enabled designs. These results demonstrate one of the significant advantages of petcoke oxy-combustion technology that utilizes CCS: CO_2 emission taxes have a relatively negligible effect on LCOE due to these technologies' ability to separate CO_2 more easily and efficiently compared to the other CCS technologies with slopes of 4.67×10^{-4} and 0.06 for the POXY CCS and POXYD designs respectively.

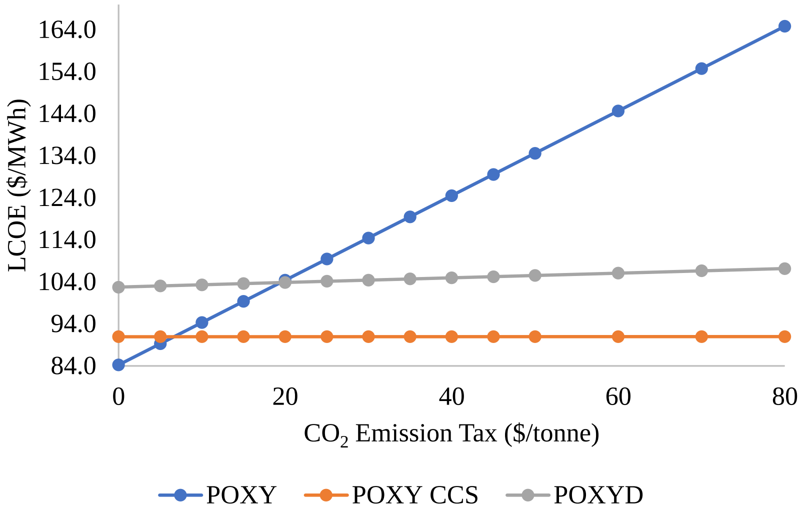

Figure 8: Sensitivity analysis of the effects of CO_2 emission tax on the LCOEs of the various petcoke oxy-combustion designs.

As expected, the LCOE of the POXY design was not affected by the cost of CO_2 T&S, as it emits all CO_2 into the environment (notably a slope of 0) as depicted in Figure 9. In contrast, the LCOEs of the POXY CCS and POXYD designs increased alongside the CO_2 T&S costs with slopes of 1.25 and 1.19 respectively. Based on the slope, it makes sense that the LCOE of the POXY CCS design increases higher compared to the POXYD design for a unit rise in cost of CO_2 T&S. This is because the POXY CCS captured (nearly 100%) and transports more CO_2 compared to the POXYD design. Nevertheless, when the CO_2 T&S cost was varied, the higher LCOE of the POXYD design is because of the high capital cost of the design compared to the POXY CCS design. For a higher cost of CO_2 T&S (say $30/tonne), the LCOE of the POXY CCS would be higher than that of POXYD design.

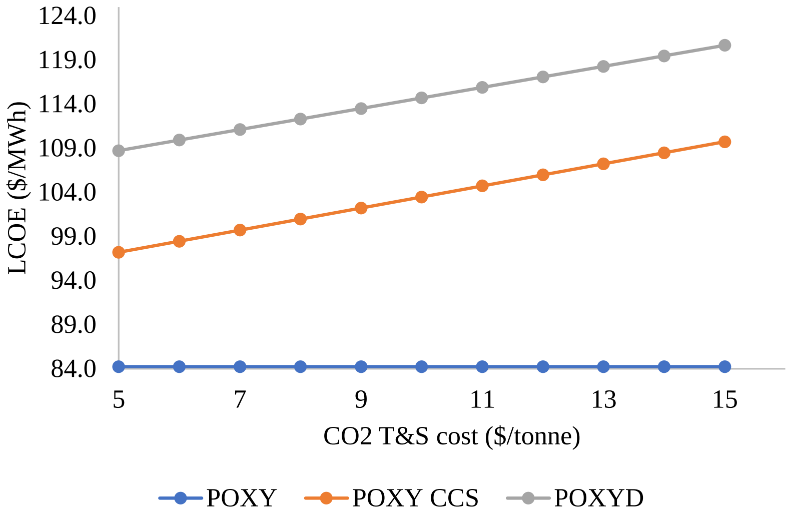

Figure 9: Sensitivity analysis of the effects of CO_2 T&S cost on the LCOE of the various petcoke oxy-combustion designs.

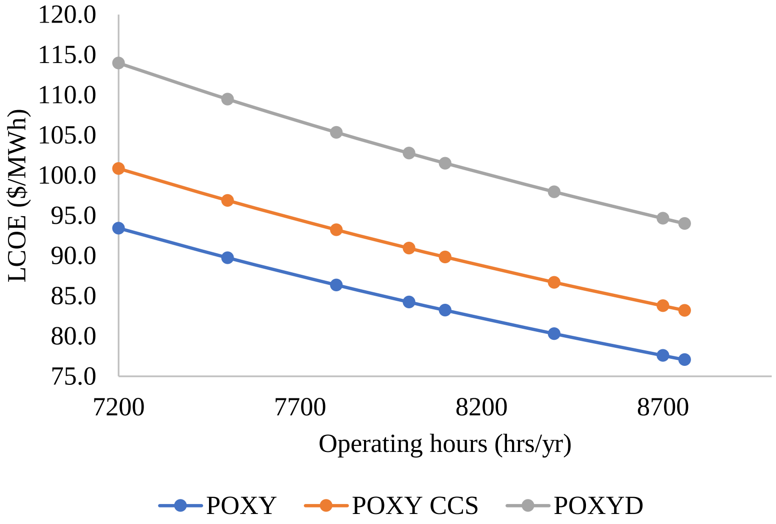

Figure 10: Sensitivity analysis of the effects of plant operating hours on the LCOEs of the various petcoke oxy-combustion designs.

Figure 10 shows how LCOE is affected when plant operating hours per annum is decreased or increased as it is varied between 7200 and 8700 hrs/yrs. Even when the operating hours are reduced to 7,200 hours per year, the POXY, POXY CCS, and POXYD designs still had LCOEs of $93.4/MWh, $100.8/MWh, and $114/MWh, respectively. Nevertheless, it is evident that power plants typically keep hours of operation that far exceed 8,000 hours per year for which these reduced operating hours (7,200 hours per year) still have competitive LCOE.

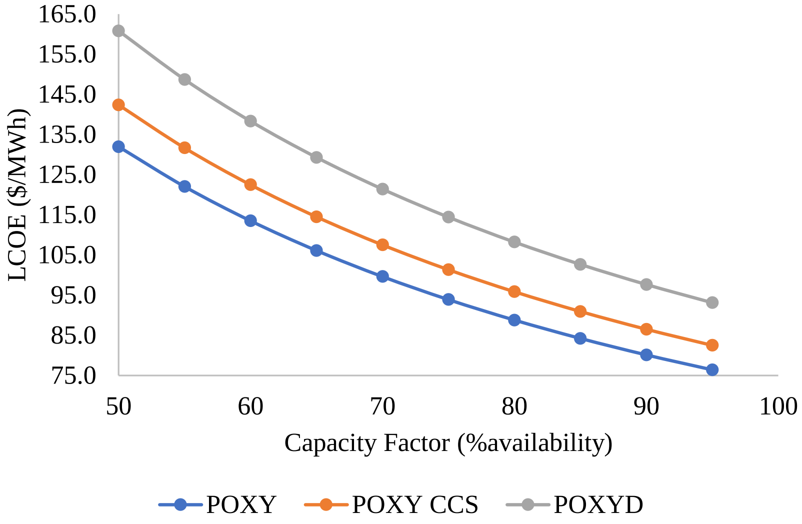

Figure 11: Sensitivity analysis of the effects of capacity factor on the LCOEs of the various petcoke oxy-combustion designs.

In analyzing operating capacity, we used a conservative base case of 85%. Moreover, we also considered how the proposed power plants performed when operated at reduced capacity, for example, at half the design capacity. The slope of the plot in Figure 11 for the POXY, POXY CCS, and POXYD designs are -1.21, -1.30, and -1.47 respectively implying a decreasing relationship. This implies that the POXYD design has the highest reduction in LCOE up to $1.47/MWh for a unit increase in the plant capacity factor. As expected, the LCOE of the proposed plant (POXYD) turned out to be $161/MWh at half the plant capacity, which represents a 56.7% increase in LCOE (Figure 11). Given this increase in LCOE, it would be highly undesired to operate under such conditions. Furthermore, during intermittent drops in operating capacity, a ramp is often used to cover for the reduced throughput and to average out the LCOE. However, the extent of this recovery in relation to uncertainty in operating capacity is beyond the scope of this study. Finally, Figure 12 shows the additional cost of operating a pressurized FGD unit as the cost of an atmospheric FGD unit was increased up to 300%. With a linear relationship, the slope of the plot is approximately 0.70 across the designs implying an increase of ¢70/MWh per unit percentage increase in the cost of the atmospheric FGD unit. Overall, at a 300% increase in the cost of the atmospheric FGD unit, the LCOE for the POXY, POXY CCS, and POXYD designs are $103.8/MWh, $110.9/MWh, and $123.3/MWh respectively for which the designs are still competitive.

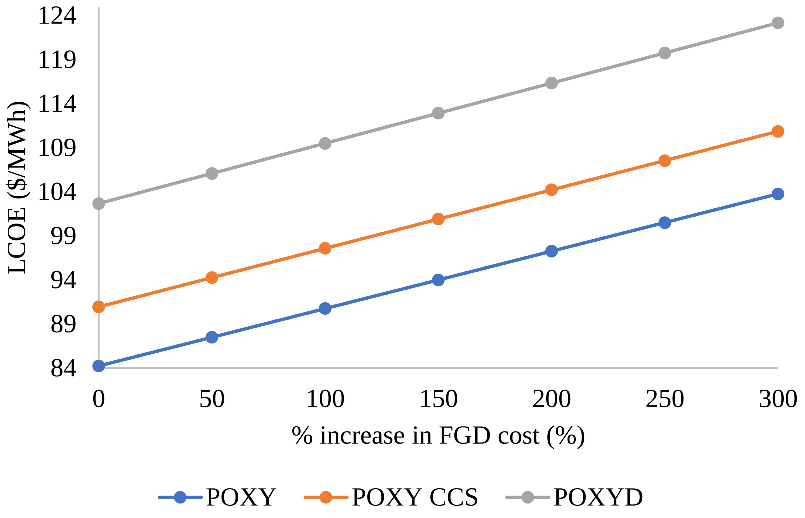

Figure 12: Sensitivity analysis of the effects of increased cost of FGD unit on the LCOEs of the various petcoke oxy-combustion designs.

4. Conclusions

This study presented and analyzed the design, GHG emissions, and cost performance of a petcoke oxy-combustion technology in order to determine its suitability as an avenue for disposing of the ever-increasing stockpiles of petcoke. To this end, this study evaluated three designs: petcoke oxy-combustion without carbon capture and sequestration (CCS), petcoke oxy-combustion with CCS, and petcoke oxy-combustion with CO_2 purification by distillation and CCS. The designs present the data used to conduct a comprehensive environmental life cycle assessment of the oxy-combustion plants which is presented in the part II of this work. Altogether, this work represents the first study to present the eco-technoeconomic and life cycle analysis that analyzed the impacts of O_2 removal from CO_2 captured from oxy-combustion exhaust via cryogenic distillation for solid fuels in general.

While the design without CCS proved to be more efficient and offered a lower levelized cost of electricity (LCOE), it also emitted more GHGs than the CCS-enabled alternatives, with CO_2 emissions of 999.3 kgCO_2/MW. Furthermore, the non-CCS design became cost-prohibitive, with an LCOE of $134.6/MWh, when a carbon emission tax was imposed. Compared to the POXYD design, the POXY CCS design provides a near 100% CO_2 capture rate, along with higher efficiency and a lower LCOE. Unfortunately, the captured CO_2 stream produced by this design possesses oxygen concentrations that exceed pipeline specifications, as high levels of oxygen can compromise pipeline integrity due to corrosion. Thus, despite being less efficient, producing higher emissions, and having a higher LCOE than its counterparts, the POXYD design was selected as the most suitable petcoke oxy-combustion technology since its sequestered CO_2 stream meets pipeline specifications. In addition, the POXYD design's cradle-to-gate GHG emissions were sufficiently lower than those of traditional coal-fired power plants, such that they provide an incentive to replace coal plants with POXYD plants for the sole purpose of reducing GHG emissions.

In the future work, an analysis that investigates the feasibility of operation of the proposed petcoke oxy-combustion designs will be evaluated. This will give rise to the study of the control strategies for efficient operation of the power plant which will help identify feasible regions of operation.

Nomenclature

Abbreviations

CAPEX	Capital expenditure
CCA	Cost of CO_2 avoided
CCS	Carbon capture and storage

DCFROR	Discounted cash flow rate of return
FGD	Flue gas desulfurization
GHG	Greenhouse gas
HEN	Heat exchanger network
HHV	Higher heating value
HPT	High-pressure turbine
HRSG	Heat recovery steam generator
IGCC	Integrated gasification combined cycle
IPT	Intermediate pressure turbine
LCOE	Levelized cost of electricity
LPT	Low-pressure turbine
OPEX	Operating expenditure
POXY	Petcoke oxy-combustion
POXY CCS	Petcoke oxy-combustion with CCS
POXYD	Petcoke oxy-combustion with CO_2 purification by distillation and CCS
ROR	Return of return

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Appendix A1: Stream conditions corresponding to Figure 1 for the POXY design

	Stream											
	1	2	3	4	5	6	7	8	9	10	11	12
T (°C)	15	32	32	31.3	25	60	552	1406	542	33	209	542
P (bar)	1	10	10	1.1	1	10	10	9.5	9.47	1	250	9.47
F (kg h^{-1})	2.12 x 10^{6}	2.12 x 10^{6}	489,386	69,067	95,716	177,912	3.58 x 10^{6}	3.87 x 10^{6}	3.87 x 10^{6}	1.27 x 10^{6}	1.46 x 10^{6}	3.09 x 10^{6}
Vapor frac.	1	1	1	1	0	Petcoke	1	1	1	0	1	1
Mass frac.												
H_2O	0.7%	0.7%			100%		19.7%	22.8%	22.8%	100%	100%	22.8%
CO_2	458 ppm	458 ppm		1.4%			60.1%	69.6%	69.6%			69.6%
Ar	1.3%	1.3%	0.8%	0.4%			0.5%	0.5%	0.5%			0.5%
H_2							41 ppm	47.45 ppm	47.45 ppm			47.45 ppm
O_2	23%	23%	99%	0.2%			16.8%	3.9%	3.9%			3.9%
N_2	75%	75%	0.3%	98%			0.5%	0.5%	0.5%			0.5%
SO_2							2%	2.7%	2.7%			2.7%
SO_3							59.9 ppm	69.4 ppm	69.4 ppm			69.4 ppm
NO_2							7.6 ppb	1.1 ppm	1.1 ppm			1.1 ppm
N_2O							41.9 ppm	8.8 ppb	8.8 ppb			8.8 ppb

Stream	13	14	15
T (°C)	552	150	150
P (bar)	10	9.47	9.47
F (kg h^{-1})	3.09 x 10^{6}	773,258	755,033
Vapor frac.	1	1	1
Mass frac.			
H_2O	22.8%	22.8%	23.5%
CO_2	69.6%	69.6%	72.9%
Ar	0.5%	0.5%	0.5%
H_2	47.45 ppm	47.45 ppm	trace
O_2	3.9%	3.9%	2.5%
N_2	0.5%	0.5%	0.5%
SO_2	2.7%	2.7%	277 ppm
SO_3	69.4 ppm	69.4 ppm	0.71 ppm
NO_2	1.1 ppm	1.1 ppm	1.1 ppm
N_2O	8.8 ppb	8.8 ppb	9.1 ppb

Appendix A2: Stream conditions corresponding to Figure 1 for the POXY CCS design

	Stream											
	1	2	3	4	5	6	7	8	9	10	11	12
T (°C)	15	32	32	31.3	25	60	552	1406	542	33	209	542
P (bar)	1	10	10	1.1	1	10	10	9.5	9.47	1	250	9.47
F (kg h^{-1})	2.19 x 10^{6}	2.19 x 10^{6}	504,747	71,235	98,721	183,496	3.70 x 10^{6}	3.99 x 10^{6}	3.99 x 10^{6}	1.31 x 10^{6}	1.51 x 10^{6}	3.19 x 10^{6}
Vapor frac.	1	1	1	1	0	Petcoke	1	1	1	0	1	1
Mass frac.												
H_2O	0.7%	0.7%			100%		19.7%	22.8%	22.8%	100%	100%	22.8%
CO_2	458 ppm	458 ppm		1.4%			60.1%	69.6%	69.6%			69.6%
Ar	1.3%	1.3%	0.8%	0.4%			0.5%	0.5%	0.5%			0.5%
H_2							41 ppm	47.45 ppm	47.45 ppm			47.45 ppm
O_2	23%	23%	99%	0.2%			16.8%	3.9%	3.9%			3.9%
N_2	75%	75%	0.3%	98%			0.5%	0.5%	0.5%			0.5%
SO_2							2%	2.7%	2.7%			2.7%
SO_3							59.9 ppm	69.4 ppm	69.4 ppm			69.4 ppm
NO_2							7.6 ppb	1.1 ppm	1.1 ppm			1.1 ppm
N_2O							41.9 ppm	8.8 ppb	8.8 ppb			8.8 ppb
Stream	13	14	15	16	17	18	19	20	21	22		
T (°C)	552	150	150	150	21	20	21	11	25	25		
P (bar)	10	9.47	9.47	9.47	9.47	1	9.37	15	84.9	153		
F (kg h^{-1})	3.19 x 10^{6}	797,805	778,359	780,424	780,424	181,982	596,383	551	595,832	595,832		
Vapor frac.	1	1	1	1	0.76	0	1	0	1	Supcri		
Mass frac.												
H_2O	22.8%	22.8%	23.5%	23.4%	23.4%	99.9%	0.1%	97.3%	337 ppm	337 ppm		
CO_2	69.6%	69.6%	72.9%	73%	73%	0.1%	95.2%	2.7%	95.1%	95.1%		
Ar	0.5%	0.5%	0.5%	0.5%	0.5%	1.13 ppb	0.7%	5.56 ppm	0.67%	0.67%		
H_2	47.45 ppm	47.45 ppm	trace	trace	trace	trace	trace	trace	trace	trace		
O_2	3.9%	3.9%	2.5%	2.5%	2.5%	7.14 ppb	3.3%	33 ppm	3.49%	3.49%		
N_2	0.5%	0.5%	0.5%	0.5%	0.5%	0.1 ppb	0.7%	2.62 ppm	0.67%	0.67%		
SO_2	2.7%	2.7%	277 ppm	281 ppm	281 ppm	182 ppm	306 ppm	511 ppm	306 ppm	306 ppm		
SO_3	69.4 ppm	69.4 ppm	0.71 ppm	0.72 ppm	0.72 ppm	0.67 ppm	0.73 ppm	3.03 ppm	0.72 ppm	0.72 ppm		
NO_2	1.1 ppm	1.1 ppm	1.1 ppm	1.1 ppm	1.1 ppm	3.84 ppm	0.29 ppm	9.85 ppm	0.28 ppm	0.28 ppm		
N_2O	8.8 ppb	8.8 ppb	9.1 ppb	9.1 ppb	9.1 ppb	trace	11.8 ppb	0.28 ppb	11.9 ppb	11.9 ppb		

Appendix A3: Stream conditions corresponding to Figure 1 for the POXYD design

	Stream											
	1	2	3	4	5	6	7	8	9	10	11	12
T (°C)	15	32	32	31.3	25	60	552	1406	542	33	209	542
P (bar)	1	10	10	1.1	1	10	10	9.5	9.47	1	250	9.47
F (kg h^{-1})	2.3×10^6	2.3×10^6	521,742	75,041	103,997	193,303	3.9×10^6	4.2×10^6	4.2×10^6	1.38×10^6	1.58×10^6	3.36×10^6
Vapor frac.	1	1	1	1	0	Petcoke	1	1	1	0	1	1
Mass frac.												
H_2O	0.7%	0.7%			100%		19.7%	22.8%	22.8%	100%	100%	22.8%
CO_2	458 ppm	458 ppm		1.4%			60.1%	69.6%	69.6%			69.6%
Ar	1.3%	1.3%	0.8%	0.4%			0.5%	0.5%	0.5%			0.5%
H_2							41 ppm	47.45 ppm	47.45 ppm			47.45 ppm
O_2	23%	23%	99%	0.2%			16.8%	3.9%	3.9%			3.9%
N_2	75%	75%	0.3%	98%			0.5%	0.5%	0.5%			0.5%
SO_2							2%	2.7%	2.7%			2.7%
SO_3							59.9 ppm	69.4 ppm	69.4 ppm			69.4 ppm
NO_2							7.6 ppb	1.1 ppm	1.1 ppm			1.1 ppm
N_2O							41.9 ppm	8.8 ppb	8.8 ppb			8.8 ppb
Stream	13	14	15	16	17	18	19	20	21	22	23	24
T (°C)	552	150	150	150	21	20	21	11	99	5.9	88	43
P (bar)	10	9.47	9.47	9.47	9.47	1	9.37	14	30	30	2.8	153
F (kg h^{-1})	3.36×10^6	840,234	818,670	820,849	820,849	191,501	627,176	560	626,615	626,615	59,079	567,498
Vapor frac.	1	1	1	1	0.76	0	1	0	1	1	1	Supcri.
Mass frac.												
H_2O	22.8%	22.8%	23.5%	23.4%	23.4%	99.9%	0.1%	97.3%	364 ppm	364 ppm	trace	401 ppm
CO_2	69.6%	69.6%	72.9%	73%	73%	0.1%	95.2%	2.7%	95.3%	95.3%	50.5%	99.9%
Ar	0.5%	0.5%	0.5%	0.5%	0.5%	1.13 ppb	0.7%	5.56 ppm	0.7%	0.7%	7.15%	0.34 ppm
H_2	47.45 ppm	47.45 ppm	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace
O_2	3.9%	3.9%	2.5%	2.5%	2.5%	7.14 ppb	3.3%	33 ppm	3.3%	3.3%	35.3%	9.4 ppm
N_2	0.5%	0.5%	0.5%	0.5%	0.5%	0.1 ppb	0.7%	2.62 ppm	0.7%	0.7%	7.1%	0.1 ppm
SO_2	2.7%	2.7%	277 ppm	281 ppm	281 ppm	182 ppm	306 ppm	511 ppm	306 ppm	306 ppm	trace	338 ppm
SO_3	69.4 ppm	69.4 ppm	0.71 ppm	0.72 ppm	0.72 ppm	0.67 ppm	0.73 ppm	3.03 ppm	0.72 ppm	0.72 ppm	trace	0.8 ppm
NO_2	1.1 ppm	1.1 ppm	1.1 ppm	1.1 ppm	1.1 ppm	3.84 ppm	0.29 ppm	9.85 ppm	0.28 ppm	0.28 ppm	0.13 ppm	0.31 ppm
N_2O	8.8 ppb	8.8 ppb	9.1 ppb	9.1 ppb	9.1 ppb	trace	11.8 ppb	0.28 ppb	11.9 ppb	11.9 ppb	5.68 ppb	12.5 ppb

Chapter 6

Application of petroleum coke disposal to electricity generation: environmental analysis of petcoke oxy-combustion.

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Advanced Petroleum Coke Oxy-Combustion Power Generation with Carbon Capture and Sequestration: Part II − Environmental Assessment and Cost of CO_2 Avoided

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Abstract

The life cycle environmental impact assessment and cost of CO_2 (CCA) avoided of a petroleum coke oxy-combustion electric power generation technology operated with and without carbon capture and sequestration are discussed. In an extension of our work on the design and economics presented in Part 1, the environmental assessment was carried out for three candidate petroleum coke oxy-combustion designs: petcoke oxy-combustion operated without carbon capture and sequestration (CCS); petcoke oxy-combustion operated with CCS; and petcoke oxy-combustion with CO_2 distillation operated with CCS. The environmental life cycle assessment of the designs was computed using both TRACI 2.1 midpoint and ReCiPe 2016 midpoint and endpoint methods. Using the levelized costs of electricity, the Cost of CO_2 Avoided was also employed as a performance metric for each of the designs. The results showed a life cycle GWP of 1089, 17.32, and 75.65 kgCO_2eq/MWh for the petcoke oxy-combustion design operated without CCS, petcoke oxy-combustion design operated with CCS, and petcoke oxy-combustion with CO_2 distillation operated with CCS respectively. It was also found that acidification potential and particulate matter emissions were higher for the petcoke oxy-combustion design operated without CCS due to the venting of SO_2 to the atmosphere. With a levelized cost of electricity between \$90.94/MWh and \$102.8/MWh, CCA of the CCS enabled designs were between \$10.43/tonneCO_2eq and \$24.35/tonneCO_2eq which is competitive with most other carbon capture options for large-scale fossil-based power plants. When the cost parameters were varied at the worst-case scenario, the highest CCA observed was \$115.9/tonneCO_2eq.

Keywords: Petcoke, Oxy-combustion, Electricity, Life cycle Analysis, CO_2 capture

1.0 Introduction

Due to government restrictions in North America on the combustion of petroleum coke (petcoke) [1], most of the petcoke which does not make its way to calcination operations are generally stockpiled. Stockpiling is considered to be the "end of life" of the petcoke, and there has been very little research into the environmental impacts of stockpiling or other disposal alternatives. In the western part of Canada with huge deposits of heavy crude oil (bitumen), coupled with the completion of the Sturgeon Refinery [2] which is designed to process diluted bitumen, more petcoke production is expected in the near future. Given the large rates of petcoke production [3], adequate on-site storage can be a challenge due to lack of room in the yards of refineries or upgraders. The business-as-usual approach requires ever-growing stockpiles in perpetuity, which is unsustainable and can have significant environmental impacts such as soil leaching and water contamination [1]. However, instead of stockpiling, petcoke can be disposed of without violating government combustion restrictions by consuming it as a fuel in an oxy-combustion process for electricity generation. Part I of this work [4] introduced three petcoke oxy-combustion variants and computed the technical and economic feasibility of each using process simulations. This work focuses on the potential environmental impacts and benefits of this approach.

Oxy-combustion employs the use of high-purity oxygen to combust fuels such as coal, natural gas, or petcoke producing nitrogen-deficient high-temperature flames which enables easy capture of the carbon dioxide in the flue gas. With this in mind, oxy-combustion technology is receiving interest as the next pathway for power generation, at least, as a replacement for the traditional supercritical pulverized coal (SCPC) power plants [5]. As the shutdown of the coal-fired power plants is anticipated in most western countries, prospects to revamp of these power plants to oxy-combustion based power plant is gaining attention [5].

There have been some life cycle analysis (LCA) studies on oxyfuel combustion, but all have focused entirely on coal-based fuels [6]. The National Energy Technology Laboratory (NETL) carried out a detailed cradle to grave LCA of the coal-based oxy-combustion power plant with carbon capture and sequestration (CCS) [7]. The analysis considered the entire emissions of coal supply chain, plant commissioning and decommissioning, and the plant operations emission. Most importantly, two scenarios that involved the storage of the captured CO_2 in a saline aquifer or for use in enhanced oil recovery (EOR) were analyzed. For the two scenarios studied, the EOR system showed to have reduced environmental impacts compared to the saline aquifer storage of CO_2 due to the displacement of natural CO_2 dome [7]. Similarly, Oreggioni et al.[8], presented a comparative environmental LCA of CCS enabled coal-fired power plants namely coal oxy-combustion, post-combustion capture with monoethanolamine (MEA), and post-combustion capture with 2-amino-2-methyl-1-propanol with piperazine (AMP/PZ). Their findings showed that there were 29% and 25% increases in the NOx emissions for the MEA and AMP/PZ plants, 24% and 20% increases in the PM emissions for the MEA and AMP/PZ plants, and a 4% and 6% increases in the SOx emissions for the MEA and AMP/PZ plants compared to the non-CCS plant (reference plant) [8]. On the contrary, the oxy-combustion plant showed an 85% decrease for NOx and a 99% decrease for both SOx and PM emissions compared to the reference plant. Pehnt et al.,[9] carried out a LCA study of lignite power plants, comparing the performance of the pre-combustion, post-combustion, and oxyfuel technologies. The results also showed that the oxyfuel technology outperformed the pre-combustion and post-combustion designs in terms of cost and greenhouse gas reductions [9]. Taken together, these studies indicate that oxyfuel combustion can have some important environmental advantages over power-combustion or pre-combustion capture strategies for CO_2 emissions reduction in coal power generation. It follows then that similar benefits are likely for petcoke-based power generation since petcoke and coal fuels are similar. However, since petcoke is a waste product, its supply chain is quite different than coal, and so we cannot use the quantitative results of the coal-based studies in the petcoke context. Therefore, a petcoke LCA must be conducted separately to ascertain its performance when compared to coal.

Thus, the objective of this work is to critically study the environmental impacts posed by the proposed petcoke oxy-combustion power plant concepts. In this work, the environmental impact categories of the three petcoke oxy-combustion power plant design configurations were evaluated and compared against petcoke integrated gasification combined cycle (IGCC), coal IGCC, and SCPC plants operated with CCS. In addition, because we performed this work under standard conditions, we then compared its economic and environmental metrics directly against almost 100 other fossil-fuel power plants with CO_2 capture, such as coal-based oxy-combustion, thermal combustion with post-combustion carbon capture with either solvents or membranes, solvent-based pre-combustion carbon capture using either gasification or reforming approaches, chemical looping combustion approaches, calcium looping capture processes, and solid oxide fuel cell (SOFC) power plants. Furthermore, our conclusions relating to the increase in costs required to remove O_2 from captured CO_2 such that it can meet pipeline specifications also indicate that the vast majority of coal-based oxy-combustion studies significantly underestimate the true costs of coal-based oxy-combustion when the captured CO_2 is pipelined.

2.0 Methodology

2.1 Life cycle methodologies

2.1.1 Goal, scope, functional unit

The main goal of this study is to compute, evaluate, and analyze the environmental impacts of employing oxy-combustion technology to produce electricity from petcoke. We consider three process variants: petcoke oxy-combustion without CCS (POXY), petcoke oxy-combustion with CCS using CO_2 purities that are traditionally used in the literature (POXY CCS), and petcoke oxy-combustion with CCS using distillation to purify the CO_2 further such that it meets existing pipeline specifications (POXYD). The POXY design presents the performance of an oxy-combustion power plant without CCS while the POXY CCS design covers the GHG emission reduction of a CCS enabled oxy-combustion power plant. Finally, the POXYD design highlights the trade-offs in cost and emissions for operating an oxy-combustion power plant whose captured CO_2 meets pipeline specifications. The reader is referred to Part I of the work for a detailed description of these processes, mass and energy balances, stream conditions, and economic analyses[4].

The scopes covered in this work include the cradle-to-plant-exit-gate (CTPG) and cradle-to-customer-gate (CTCG) material and energy inputs and outputs, with their corresponding emissions over the life cycle of the petcoke oxy-combustion plants, and with analysis boundaries illustrated in Figure 1. This includes the operation of the power plant, its commissioning and decommissioning, and the disposal of solid ash wastes from it. The scope also includes transmission and distribution losses of electricity and its associated emissions but does not include the final use of electricity as it is not easily quantified. For the POXY CCS and POXYD cases, the scope also includes CO_2 transportation to a sequestration site via pipeline, the associated leaks, and the commissioning, and decommissioning of the pipeline. We chose the functional unit to be 1 MWh of electricity, AC, delivered, low voltage, which uses the CTCG system boundary.

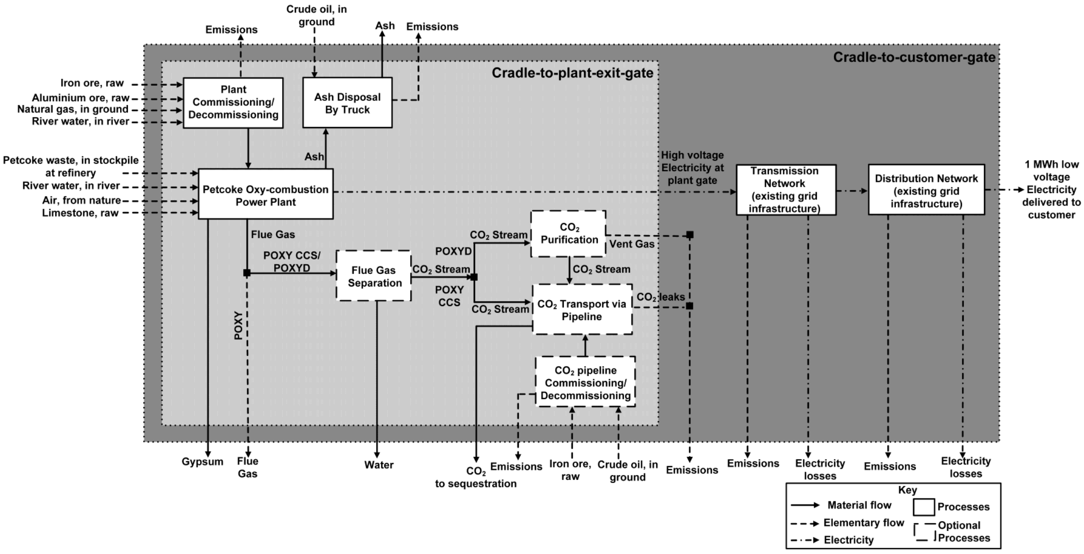

Figure 1: Superstructure of the system boundary of the three proposed petcoke oxy-combustion processes of interest. The solid boxes apply to all three cases (POXY, POXY CCS, and POXYD) and the dashed boxes only apply to cases with CO$_2$ capture (POXY CCS and POXYD).

2.1.2 Life cycle inventory methods and assumptions

Stockpiled petcoke was used as the feed for the proposed oxy-combustion technology designs. Petcoke is a waste product of the oil refinery process; thus, there was no indirect emission attributed to petcoke [10]. We assumed that the proposed petcoke oxy-combustion design would be situated in an existing refinery in Alberta, Canada; thus, neither land-use change nor transportation from the site of waste generation to the oxy-combustion facility was considered in this work. The type and properties of the petcoke feedstock used in this analysis are given in Table 1 and for brevity, the petcoke metal composition is provided in the supplementary document. The material consumption, energy demand, electricity production, and emissions generated from each petcoke oxy-combustion process was taken from Part I of this work [4]. Additional data used for this LCA study can be found in the supplementary document of this manuscript, which includes details of the material input and output.

Table 1: Properties of delayed coke [11].

Delayed coke			
HHV (MJ/kg)	34.7		
Ultimate analysis (wt. % dry)			
C	84.9	Cl	0
H	3.9	Ash	3.1
N	1.3	O (diff)	0.8
S	6		
Proximate analysis (wt. %)			
Moisture	1.8	Fixed carbon	83.3
Volatile matter	11.9	Ash	3

2.1.3 Impact assessment methods

Common life cycle impact assessment calculation methods include TRACI, ReCiPe 2016, ILCD, CML. Each calculation method estimates the impact of a chemical compound based on a stressor using different characterization factors. There is no single impact assessment calculation method that is all encompassing or superior to the others. In this study, we used both TRACI 2.1 and ReCiPe 2016 calculation methods. TRACI was chosen as it is well suited for North American

LCA studies with the impact category results presented at the midpoint level only. The TRACI impact categories considered in this study are shown in Table 2.

Table 2: TRACI v2.1 midpoint impact categories considered in this study.

Impact category	Abbreviation	Units
Midpoint		
Ozone depletion potential	ODP	kg CFC-11eq
Global warming potential	GWP	kg CO_2 eq
Smog formation	SF	kg O_3 eq
Acidification potential	AP	kg SO_2 eq
Eutrophication potential	EP	kg N eq
Carcinogenics potential	CP	CTUh
Non-carcinogenics potential	NCP	CTUh
Respiratory effects	RE	kg PM2.5 eq
Ecotoxicity potential	ETP	CTUe
Fossil fuel depletion	FFD	MJ surplus

Unlike the TRACI method which is intended specifically for North American studies, the recent ReCiPe 2016 calculation method whose characterization factors are representative of a global scale was also presented. The ReCiPe method presents impacts in three levels of perspectives namely individualist, hierarchist, and egalitarian, and the reader is directed to Huijbregts et al.[12] for more information on these perspectives. In this work, we chose the hierarchist perspective which uses an average time horizon of 100 years and is representative of a balance between short term and long-term interests. The results for the other two perspectives are available in the supplementary material. Table 3 shows the ReCiPe 2016 midpoint and endpoint impact categories that were considered in this study, along with their corresponding extent or area of impact.

Table 3: ReCiPe 2016 midpoint and endpoint impact categories considered in this study.

Impact category	Abbreviation	Units
Midpoint		
Global warming potential	GWP	kg CO_2 eq
Stratospheric Ozone depletion	SOD	kg CFC-11eq
Fine particulate matter formation	FPMF	kg PM2.5 eq

Ozone formation	OF	kg NO_x eq
Terrestrial acidification	TA	kg SO_2 eq
Marine eutrophication	ME	kg N eq
Terrestrial ecotoxicity	TET	kg 1, 4-DCB
Freshwater ecotoxicity	FWET	kg 1, 4-DCB
Marine ecotoxicity	MET	kg 1, 4-DCB
Human carcinogenic toxicity	HCT	kg 1, 4-DCB
Human non-carcinogenic toxicity	HNCT	kg 1, 4-DCB
Fossil resource scarcity	FRS	kg oil eq
Water consumption	WC	m^3
Endpoint		
Damage to human health	HH	DALY
Damage to ecosystem diversity	ED	Species-yr
Damage to resource availability	RA	$

2.1.4 Calculation strategy and comparisons against competing concepts

For both TRACI 2.1 midpoint and ReCiPe 2016 midpoint and endpoint assessment methods, we used the SimaPro v9.0[13] LCA modeling software to model and compute the environmental impacts of each design. Since limited information is available on petcoke-based oxy-combustion processes, the results of this work were compared against data available in the literature for three coal-based processes. The first is coal-based oxy-combustion, from which data were taken from the work of Adams et al. [14] The work presents data for more than 20 techno-economic analysis studies presented in the literature which have been converted to standard conditions, such as a uniform power plant output, uniform geographical location, uniform supply chain assumptions, uniform market prices, and other important conditions. The economic conditions used in the present work (as determined in Part I) use the same standard conditions as [14]. Similarly, the GWP method used in [14] is the same as in both the TRACI 2.1 and ReCiPe 2016—Heirarchist perspective methods used in this work (the International Panel of Climate Change 5th Assessment Report's "100 year" GWP metric).

The other two coal-based processes considered for comparison are SCPC with CCS and IGCC with CCS. Detailed life cycle inventory data for these processes are available from Nease et al. [15] which use essentially the same system boundaries and assumptions as the present work.

Because Nease et al. used the now outdated ReCiPe 2008 method, we recomputed the life cycle impact assessment characterization factors using the ReCiPe 2016 method (Hierarchist perspective) for consistent comparison with the present work.

2.2 Process description

2.2.1 Petcoke oxy-combustion power plant

The refinery waste stockpiled petcoke is fed to the oxy-combustor in slurry form (crushed and mixed with water) in the presence of 98 mol% pure oxygen at a stoichiometric ratio, or just slightly above it. Thus, combustion reaction takes place producing carbon dioxide and steam rich hot flue gas with other constituent gases such as O_2, N_2, Ar, SO_2, and SO_3 in small proportion. To control the temperature of the oxy-combustion, some portion of the flue gas is recycled into the combustor. Steam at subcritical and supercritical conditions are produced by recovering heat from the hot flue gas at the heat-recovery steam generator (HRSG). Electricity is then produced by passing the produced steam through a combination of a high-pressure turbine (HPT), an intermediate pressure turbine (IPT), and a low-pressure turbine (LPT), respectively via superheater, deaerator systems. The flue gas desulfurization (FGD) unit is employed, with the aid of limestone slurry, to remove sulfide impurities in the remaining unrecycled flue gas, producing gypsum in the process. As there exists only a small amount of nitrogen in the system, a de-NOx step is not required, and so NOx formation is minute.

2.2.2 Flue gas separation

Unlike the POXY design, the POXY CCS and POXYD designs employ a three-stage flash drum sequence to separate the CO_2 and H_2O rich streams. The separated water stream is 99.9mol% pure that it can be used in the process to reduce the water burden of the system. The captured CO_2 is compressed to supercritical conditions and then pumped to 153 bar for transport to the CO_2 sequestration site. However, based on some known CO_2 transportation pipeline O_2 tolerance limits [16], the CO_2 stream contains up to 3% O_2 at the plant exit gate, which is undesirable as it has the tendency to corrode the CO_2 pipeline [17]. Having noticed that most coal-based oxy-combustion studies in the open literature did not remove the excess O_2 in the CO_2 stream, the POXY CCS design is presented for ease of comparison.

2.2.3 CO_2 purification by distillation

To further purify the CO_2 stream to reduce the O_2 concentration to an acceptable pipeline limit, the POXYD design employs cryogenic CO_2 purification via distillation operation prior to compression for pipeline transport. This subprocess uses a collection of integrated heat exchangers to minimize the refrigeration duty requirements of the O_2/CO_2 distillation column. While the excess heat from the process is sufficient for satisfying the reboiler duty, the condenser duty is provided by the propane refrigeration cycle. The refrigerant was cooled by creating a pressure drop across the valve based on the Joule-Thompson effect. Instead of a near 100% capture rate achieved in the POXY CCS design, a 95% CO_2 capture was targeted in this design as it allowed for more feasible costs and refrigeration duties. This implies the venting of this CO_2 alongside the removed O_2 to the atmosphere constituting a direct CO_2 emission from the process. Overall, the O_2 content in the captured CO_2 stream is less than 10 ppm which satisfies the pipeline standard [16]. Finally, the CO_2 stream with a CO_2 concentration of 99.9% is pumped to supercritical condition and subsequently to 153 bar.

2.2.4 Plant commissioning

We considered the impacts of the materials and energy inputs required to construct the petcoke oxy-combustion plants. Data for the commissioning and decommissioning of the plants alongside the associated emissions for all the plant designs were all estimated from an NETL study [18].

2.2.5 Ash disposal

The impacts of disposing of ash produced during petcoke oxy-combustion were considered in this work. Specifically, the ash disposal operation primarily involves the emissions for the use and combustion of diesel in industrial equipment used to transport the ash. We used the NETL ash disposal data in this work [19].

2.2.6 CO_2 transport pipeline construction

For the designs that incorporated CO_2 capture which is not an integral part of a power plant, the material and energy inputs together with the emissions associated during the construction and decommissioning of a CO_2 transportation pipeline were estimated based on a prior NETL study [20] for a 160 km distance and expressed on the basis of kg of CO_2 transported. In addition to the construction and decommissioning emission, fugitive CO_2 leaks during transportation were also included in this analysis. As the power plant is assumed to be located near an existing oilsands project in Alberta, this study assumes the use of the Quest carbon capture and storage facility in Alberta [21] with an estimated distance of 151 km from the proposed petcoke oxy-combustion plant as the location for the CO_2 storage. We assumed a 1% leakage for the transported CO_2 [22]**.**

2.2.7 Electricity transmission

Exiting the oxy-combustion plant gates for the different designs considered in this study, the produced electricity is transmitted through the grid to the customer location. In this study, we assumed that the electricity is transmitted using the existing grid infrastructure. Thus, emissions accrued from the commissioning and decommissioning of electricity grid transmission lines (infrastructure) are not considered. Nevertheless, we considered the emissions incurred due to electricity transmission losses. Based on the report of Skone et al., [23] an average transmission loss of 3.05% was used in this study. In addition, the sulfur hexafluoride transmission emissions were also considered [23].

2.2.8 Electricity distribution

To deliver electricity to end-users, the distribution lines which operate at low voltages compared to the transmission lines that operate at high voltages are used. This study assumes that a secondary distribution of electricity which delivers electricity to commercial or residential consumers [24] was employed. Electricity distribution losses of up to 5.56% of the distributed electricity were considered in this analysis. As mentioned for the transmission infrastructure, emissions accrued from the commissioning and decommissioning of electricity distribution lines and stations were not accounted for.

2.3 Cost of CO_2 Avoided

We calculated the cost of CO_2 avoided (CCA) of the proposed petcoke oxy-combustion power plants to understand how expensive it is to avoid CO_2 emissions by choosing to construct a petcoke oxy-combustion with CCS process specifically for environmental purposes. For brevity, details of the cost estimation including the equipment sizing, equipment costs, total capital investment (TCI), operating costs (OPEX) can be found in the designs and economics study presented in Part I of this work [4]. Furthermore, in Part I, the levelized cost of electricity (LCOE) was calculated for the power plants with and without CCS.

The economic analysis of the CCS technology implemented in the proposed oxy-combustion systems was conducted using the metric of CCA, which captures the extra costs incurred by the power plant in minimizing CO_2 emissions. The formula for CCA is given in equation 1:

$$CCA = \frac{(LCOE_{CCS,design} - LCOE_{Ref\_plant})}{(GHG_{Ref\_plant} - GHG_{CCS,design})} \qquad (1)$$

where $LCOE_{Ref\_plant}$ and GHG_{Ref_plant} are the LCOE (in \$US2016 per MWh) and CTPG GHG emissions (in tCO_2eq per MWh of net power output) of the reference plant, and $LCOE_{CCS,design}$ and $GWP_{CCS,design}$ are the LCOE (in \$US2016 per MWh) and CTPG GHG emissions (in tCO_2eq per MWh of net power output) of the candidate CCS-enabled designs. To enable comparison, the CTPG boundary GHG emissions of the petcoke oxy-combustion was used for the calculation of CCA to be consistent with that reported by the reference and other power plants. Again, all plants considered and the reference case are sized to 550 MW net power output.

A US bituminous supercritical pulverized coal power plant without CO_2 capture and a net plant capacity of 550 MW was used as the reference plant for this study. The GHG and LCOE of the reference plant used in this study are 944.4 $kgCO_2eq/MWh$ and \$81.1/MWh respectively [25]. It assumes that a new petcoke plant with CCS at 550 MW net production (at the plant gate) would be constructed instead of a new a pulverized coal power plant without CCS, also at 550 MW. This plant was selected because it is a commonly chosen point of reference making it very useful for cross-technology comparisons and analysis. It is important to distinguish between the CCA definition used above and other forms, such as if the reference plant is the same process but without CCS. In the latter case, the comparison would be better termed "the cost of CO_2 capture" rather than CCA, and the reader is referred to Adams et al. [14] for a discussion as to why this is not the appropriate metric to use for this analysis. Other alternatives for the reference case may be more appropriate in case-specific circumstances, such as the local electricity grid mixture, a new power plant of a different type, or the destruction of an existing power plant.

3.0 Results

3.1 TRACI calculation results

The results of the CTCG life cycle inventory for the proposed petcoke oxy-combustion technologies with and without CCS are shown in Table 4. Generally speaking, designs with more parasitic load associated with various stages of CO_2 capture have more non-CO_2 emissions, such as ammonia, benzene, toluene, ethylbenzene, and xylene (BTEX), carbon monoxide, methane, nitrogen oxides, particulates, and other volatile organic compounds. However, POXY has higher emissions of sulfur dioxide (SO_2) compared to POXY CCS and POXYD because the SO_2 produced was small enough to be captured along with the CO_2 without violating the CO_2 pipeline specifications. The SF_6 emissions are the same for all designs since these emissions emanate from losses in electricity during transmission, which is the same for all of the plants, as they deliver the same amount of electricity. POXYD has a higher parasitic load, a lower efficiency, and a lower CO_2 capture rate compared to POXY CCS, and so it has higher CO_2 emissions and higher emissions of many other chemical emissions associated with its larger supply chain. However, POXYD actually had lower emissions for certain chemicals. As shown in Table 4, there were higher amounts of ammonia, dinitrogen monoxide, lead, mercury, and methane emissions for the POXY CCS design compared to the POXYD design. This is because the CO_2 pipeline for POXY CCS is larger than POXYD, and so the indirect impacts of pipeline commissioning (particularly from iron ore and crude oil consumption) for the plant life time of 30 years outweigh the upstream benefits for those chemicals.

Table 4: CTCG inventory data for the petcoke oxy-combustion technologies with and without CCS, for a basis of 1 MWh electricity delivered, AC, low-voltage

Inventory	POXY	POXY CCS	POXYD
Input flows (kg unless otherwise specified)			
Petcoke waste, in stockpile, at refinery	323	334	351
Air, from nature	3866	3976	4188
Iron ore, raw	2.81×10^{-3}	2.74	2.62
Aluminium ore, raw	2.21×10^{-3}	2.21×10^{-3}	2.21×10^{-3}
Natural gas, in ground (MJ)	5.26	5.26	5.26
Crude oil, in ground (MJ)	2.69	22.60	21.8
River water, in river	1491	1538	1751

Output flows			
Products flow			
Electricity delivered, AC, low-voltage (MWh)	**1**	**1**	**1**
Sequestered CO_2 (kg)	0	1083	1032
Emissions flow to air (kg)			
Ammonia	1.77×10^{-6}	1.63×10^{-4}	1.55×10^{-4}
Arsenic	1.93×10^{-8}	1.95×10^{-8}	2.01×10^{-8}
BTEX	3.51×10^{-6}	3.63×10^{-6}	3.81×10^{-6}
Carbon dioxide	1086	15.3	73.7
Carbon monoxide	1.07×10^{-2}	1.10×10^{-2}	1.10×10^{-2}
Dinitrogen monoxide	1.80×10^{-5}	3.68×10^{-5}	3.64×10^{-5}
Lead	8.42×10^{-8}	1.24×10^{-7}	1.23×10^{-7}
Mercury	1.34×10^{-8}	3.75×10^{-8}	3.66×10^{-8}
Methane	1.05×10^{-3}	2.90×10^{-3}	2.83×10^{-3}
Nitrogen oxide	2.59×10^{-3}	2.67×10^{-3}	2.75×10^{-3}
Particulates, > 2.50 µm, and < 10 µm	1.01×10^{-4}	1.33×10^{-4}	1.34×10^{-4}
Sulfur dioxide	4.14×10^{-1}	6.85×10^{-2}	7.19×10^{-2}
Sulfur hexafluoride (SF_6)	8.16×10^{-5}	8.16×10^{-5}	8.16×10^{-5}
VOC, volatile organic compounds	1.19×10^{-4}	1.21×10^{-4}	1.23×10^{-4}

Table 5 shows the TRACI 2.1 midpoint CTCG life cycle impact assessments for the three petcoke oxy-combustion technologies operated with and without CCS. The limitation of the CCS technology is in the increased environmental impacts as seen in the increased impact categories of the POXY CCS and POXYD designs. These are observed in the lower ozone depletion potential (ODP), smog formation (SF), eutrophication (EP), carcinogenics potential (CP), non-carcinogenics potential (NCP), ecotoxicity (ETP), and fossil fuel depletion (FFD) impact categories of the POXY design. On the contrary, the acidification potential (AP) and respiratory effects (RE) categories for the non-CCS design (POXY) showed to be higher than the CCS-enabled designs. The increased AP of the POXY compared to the POXY CCS and POXYD designs is because of the high SO_2 released to the atmosphere in the POXY design compared to the POXY CCS and POXYD designs whose SO_2 found its way into the CO_2 pipeline. It is worthy to note that although SO_2 enters the pipeline, there are no recommended specifications for the SO_2 in the pipeline [16], and so we assumed that it is small enough that it does not compromise the integrity of the pipeline. For RE, even though the particulates emission of the POXY CCS and POXYD designs are higher than the POXY design, they still have 83.1% and 82.3% lower respiratory effects respectively than the POXY design. Such observation is still tied to the SO_2

vented to the environment which is a chemical stressor for respiratory effects. The life cycle GHG emissions of the POXY, POXY CCS, and POXYD designs are 1089 kgCO_2eq/MWh, 17.32 kgCO_2eq/MWh, and 75.65 kgCO_2eq/MWh respectively.

Table 5: TRACI v2.1 CTCG midpoint LCA results for the petcoke oxy-combustion power plants, for a basis of 1 MWh electricity delivered, AC, low-voltage.

Impact category	Units	POXY	POXY CCS	POXYD
Ozone depletion	kg CFC-11eq	5.55×10^{-9}	6.22×10^{-9}	6.20×10^{-9}
Global warming	kg CO_2 eq	1089	17.32	75.65
Smog formation	kg O_3 eq	9.83×10^{-2}	0.108	0.111
Acidification	kg SO_2 eq	0.421	7.47×10^{-2}	7.82×10^{-2}
Eutrophication	kg N eq	1.09×10^{-2}	1.12×10^{-2}	1.12×10^{-2}
Carcinogenics	CTUh	2.79×10^{-8}	7.88×10^{-7}	7.52×10^{-7}
Non carcinogenics	CTUh	1.51×10^{-7}	4.89×10^{-7}	4.74×10^{-7}
Respiratory effects	kg PM2.5 eq	2.54×10^{-2}	4.28×10^{-3}	4.49×10^{-3}
Ecotoxicity	CTUe	2.52	10.29	9.95
Fossil fuel depletion	MJ surplus	0.79	22.10	21.11

As depicted in Figure 2, ODP is primarily caused by the oxyfuel commissioning which accounts for the emissions emanating from the materials and energy consumed during plant construction. POXY CCS and POXYD had 12.1% and 11.6% higher ODP respectively than POXY largely due to CO_2 pipeline construction. 99.7% of the life cycle GHG emissions for the POXY design was due to direct plant operation emissions, whereas for the POXY CCS and POXYD designs, direct plant operation emissions accounted about 4% and 79% of the total GHG emissions respectively. The contribution is low for POXY CCS because the design is capable of capturing nearly 100% of the direct CO_2 emissions [4]. Plant operation emissions, plant construction, and ash disposal are responsible for SF tendency of the POXY design while CO_2 transport in addition to those of POXY design causes SF for the POXY CCS and POXYD. In all the designs studied, AP and RE are primarily caused by SO_2 in the direct plant emissions. For the EP, CP, NCP, and ETP impact categories, while plant construction is the primary contributor of such impact in the POXY design (being that plant construction constitutes up to 59% of direct fossil energy consumption), CO_2 pipeline construction is chiefly responsible for those emissions for the POXY CCS and POXYD designs. Finally, the FFD tendency of the POXY design is from plant construction, direct plant operation, and ash transport which accounts for 59%, 27%, and

13% respectively. In the CCS-enabled design, CO_2 pipeline construction showed to dominate the fossil energy utilization of the POXY CCS and POXYD plants. This is not surprising as it consumes 0.018 MJ (in HHV) of fossil fuel per kg CO_2 transported for which in this study, more than 1 tonne of CO_2 is transported and sequestered for both POXY CCS and POXYD.

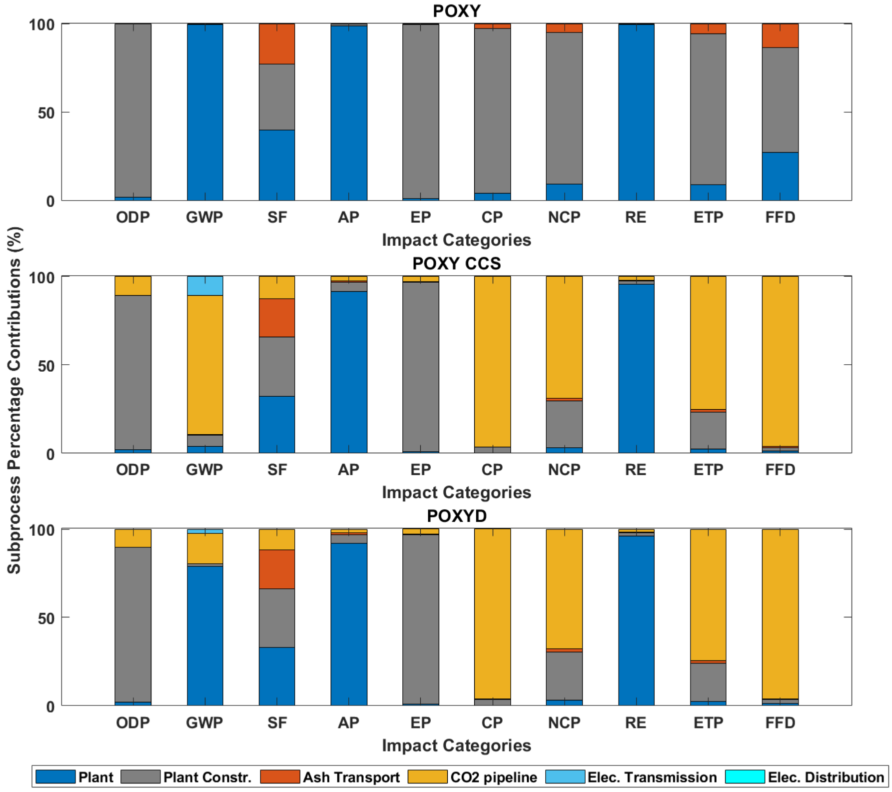

Figure 2: Contributions plot of the CTCG LCA of the proposed CCS-enabled petcoke oxy-combustion designs against the petcoke IGCC

3.2 ReCiPe calculation results

The LCIA results of the petcoke oxy-combustion plants calculated using ReCiPe 2016 method for the hierarchist (H) perspective are presented in Table 6. As mentioned earlier, unlike the TRACI 2.1 method, the ReCiPe LCA method estimates the impact categories using the world averages for normalization factors. Nevertheless, the same environmental impact trends observed for the three petcoke oxy-combustion power plant configurations using TRACI 2.1 was also observed using the ReCiPe 2016 method. The GWP for the non-CCS design is between 14.3 and 61.8 times higher than the CCS enabled designs. Similarly, due to the SO_2 vented to the environment, the FPMF, TA, and ME are quite high for POXY compared to POXY CCS and POXYD which ends up in the pipeline. Besides these, POXY had lower impacts compared to POXY CCS and POXYD which is the trade-off for the CCS technology.

Table 6: Recipe 2016 CTCG midpoint characterization results (H perspective) for the petcoke oxy-combustion designs, for a basis of 1 MWh electricity delivered, AC, low-voltage.

Impact Category	Units	POXY	POXY CCS	POXYD
Global warming potential	kg CO_2 eq	1089	17.6	75.9
Stratospheric ozone depletion	kg CFC-11eq	2.0×10^{-7}	4.1×10^{-7}	4.06×10^{-7}
Fine particulate matter formation	kg PM2.5 eq	0.122	2.12×10^{-2}	2.22×10^{-2}
Ozone formation	kg NOx eq	2.77×10^{-3}	3.16×10^{-3}	3.22×10^{-3}
Terrestrial acidification	kg SO_2 eq	0.419	7.30×10^{-2}	7.64×10^{-3}
Marine eutrophication	kg N eq	3.12×10^{-3}	3.19×10^{-3}	3.18×10^{-3}
Terrestrial ecotoxicity	kg 1, 4-DCB	1.45×10^{-2}	0.20	0.19
Freshwater ecotoxicity	kg 1, 4-DCB	4.38×10^{-4}	1.12×10^{-2}	1.13×10^{-2}
Marine ecotoxicity	kg 1, 4-DCB	5.88×10^{-4}	1.64×10^{-4}	1.65×10^{-4}
Human carcinogenic toxicity	kg 1, 4-DCB	9.25×10^{-5}	2.15×10^{-3}	2.15×10^{-3}
Human non-carcinogenic toxicity	kg 1, 4-DCB	2.13×10^{-2}	0.66	0.65
Fossil resource scarcity	kg oil eq	5.65×10^{-2}	6.51	6.21
Water consumption	m^3	1.62	1.67	1.90

To compare the performance of the proposed petcoke oxy-combustion against more commonly studied the state-of-art systems, we considered the environmental impacts of IGCC and SCPC plants operated with CCS, using the LCIA data from Nease et al. [15], as well as the petcoke-powered IGCC with CCS plant presented in our prior work [26]. For a fair comparison, we ensured that both studies used equivalent cradle-to-customer-gate boundaries, including the transmission of electricity, voltage step-down, and captured CO_2 transportation. Figure 3 depicts the comparison for which the results are normalized relative to the impacts of the SCPC plant in each category. As can be seen, the petcoke oxy-combustion designs had lower GWP than the petcoke IGCC, IGCC, and SCPC plants. Apart from the FPMF and TA impact categories for which the petcoke oxy-combustion plants showed to have higher impacts, the SOD, OF, ME, FWFT, MET, HCT, HNCT, and FRS of the petcoke oxy-combustion designs had lower impact than the other designs. These impacts are much higher for the coal-based systems, which is attributable to the upstream coal extraction and transportation emissions. Secondly, the high parasitic load of the solvent-based CCS technology utilized by the IGCC and SCPC plants necessitates the consumption of higher amounts of feed (coal or petcoke) per unit electricity produced. The higher FPMF and TA impacts of the petcoke oxy-combustion designs compared to the petcoke IGCC design are attributed to the nature of the gasification process for which the oxy-combustion process produces NOx and SOx compared to the gasification technology. For water depletion, the water consumption (WC) of the petcoke oxy-combustion power plant completely outperforms the SCPC plant. When compared to the coal IGCC plant, at least a 28% reduction in WC was observed confirming the benefits of the proposed oxy-combustion technology.

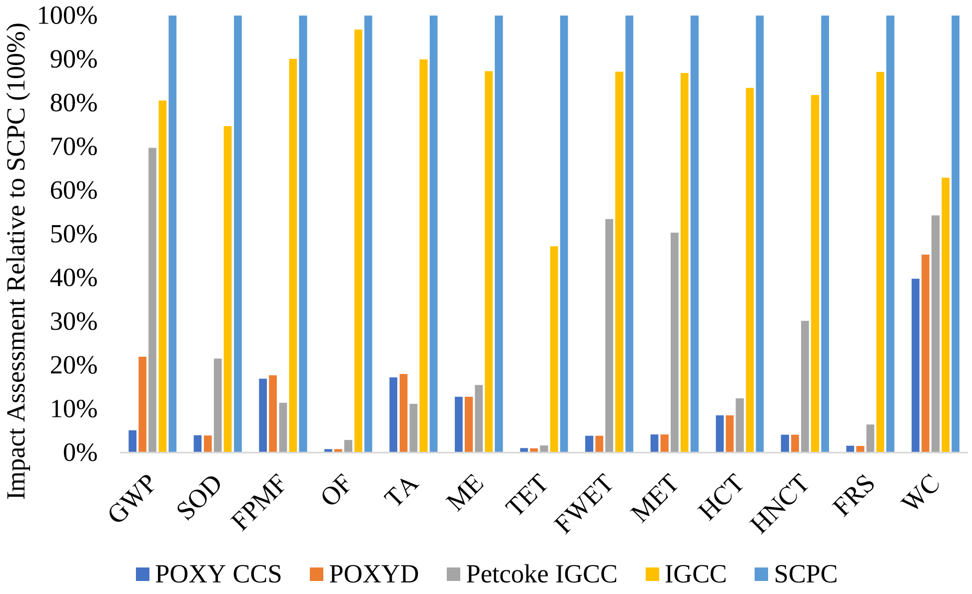

Figure 3: Comparative CTCG LCA of the proposed CCS-enabled petcoke oxy-combustion designs against the petcoke IGCC, coal IGCC, and SCPC plants relative to SCPC plant. All cases considered have CCS-enabled systems. Coal IGCC and SCPC data were obtained from [15] and petcoke IGCC data was obtained from [26]

The ReCiPe 2016 endpoint environmental impacts of the petcoke oxy-combustion designs with CCS were also compared as shown in Figure 4. The human health impacts, which are predominately due to GHG emissions as opposed to other factors like carcinogens, vastly outweigh the other categories when weighted according to the normalization factors in ReCiPe 2016. As a result, the total endpoint impacts tend to mirror the GHG emissions of each design option, with POXY CCS and POXYD by far the lowest overall impact. Ecosystem diversity, although relatively smaller than human health impacts, is also dominated by GHG emission impacts, and follows the same trends. Resource availability is a small impact compared to the others. Overall, the endpoint results show that GHG emissions dominate environmental emissions in large measure compared to other kinds of impacts. Taken on the whole, the POXY CCS and POXYD designs generally had the far superior environmental performance to the other approaches, and as noted in Figure 5, equal or lower LCOE as well. This makes the petcoke approach very promising.

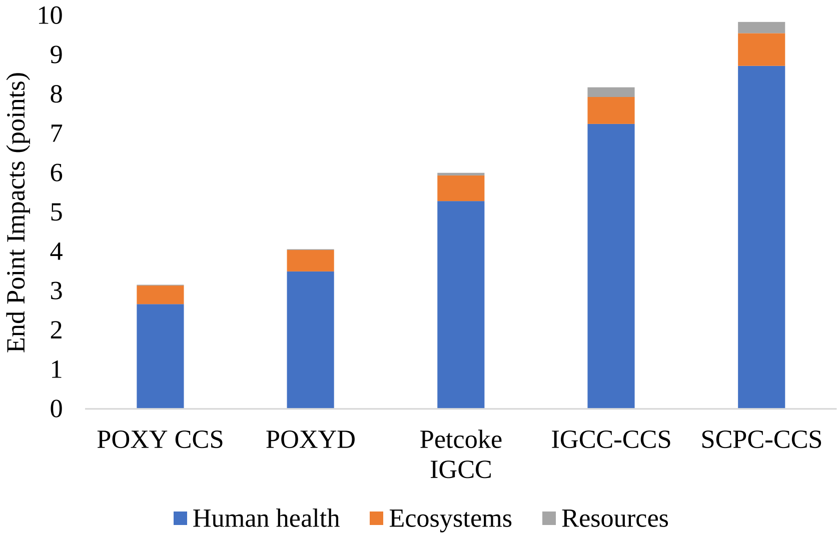

Figure 4: Endpoint impact for the petcoke oxy-combustion compared to the petcoke IGCC, coal IGCC, and SCPC plants.

3.4 Comparative LCOE vs GHG performance analysis

Next, we compared the performance of our proposed petcoke oxy-combustion designs with CCS to other fossil-fuel-based power-generation technologies with CCS, particularly the coal-based oxy-combustion technologies that were presented in our previous meta-study [14]. The results of this comparison are shown in Figure 5. In order to enable a big-picture comparison of these various power-generation technologies, we plotted our petcoke oxy-combustion data on the LCOE vs GHG emissions scatter plot presented in Adams et al. [14]. Each point in this plot represents the LCOE and cradle-to-product GHG emissions of nearly 100 techno-economic analyses presented in the literature for nine different kinds of power plants as adjusted by Adams et al. [14] to convert as-reported results in each paper into adjusted values which are based on standardized analysis parameters such as net power output, fuel supply chains with corresponding life cycle impacts, fuel cost, geographical region of operation, and year of construction—standards which were used in the present study as well. Most of the points on this plot were determined in the prior work, and so the reader is referred to that paper for a more detailed analysis. Instead, we focus on the new points on the plot, which are the POXY CCS and POXYD results of this work, as well as an additional petcoke IGCC plant taken from [26] for additional context. We note that for this plot, the LCOEs of the POXY CCS and POXYD were taken from Part I of this work [4] and the corresponding GHG emissions used the cradle-to-gate-exit boundary (where the product is electricity, AC, high-voltage) shown in Figure 1 in order to be consistent with the boundaries selected in [14].

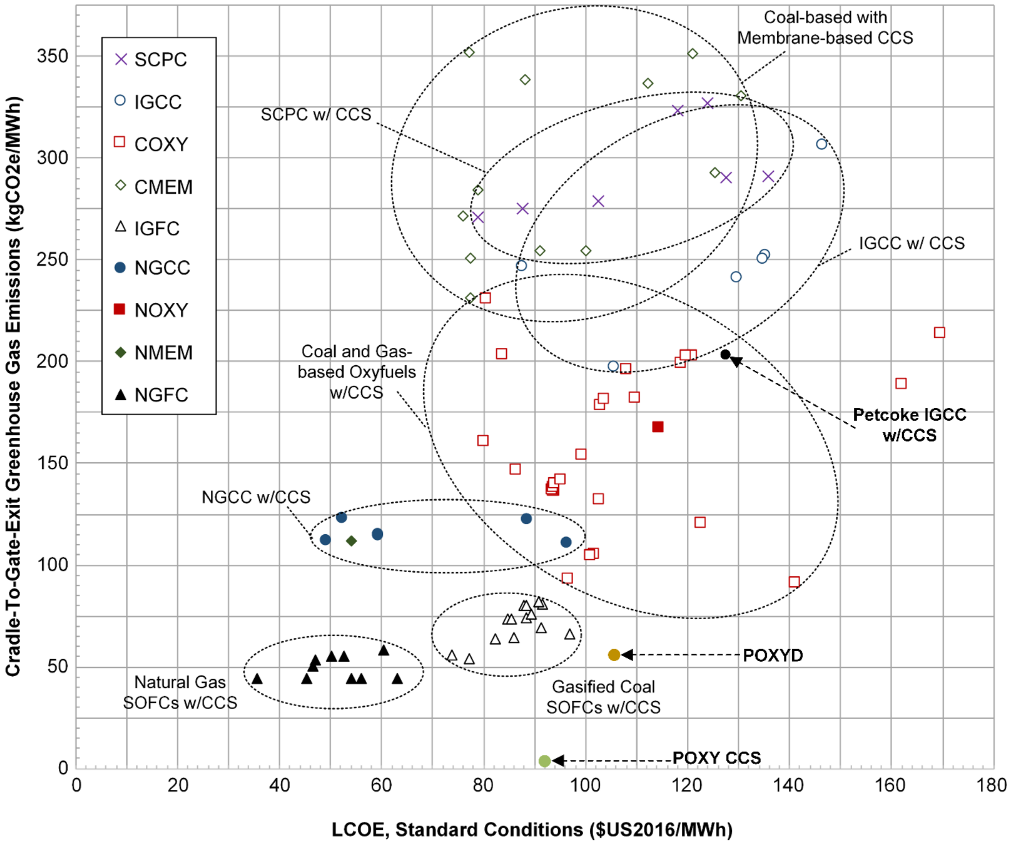

Figure 5: Scatter plot of LCOE vs. GHG emissions depicting the comparative performances of the proposed petcoke oxy-combustion technology and various coal and natural gas power-generation technologies. Each point in the plot resulted from a techno-economic analysis and life cycle analysis for a power plant with CCS enabled. Adapted from Adams et al. [14] with data added from the present work and [26]. COXY = coal-based oxyfuels, CMEM = coal-based membranes, IGFC = integrated gasification (solid oxide) fuel cell, NGCC = natural gas combined cycle, NOXY = natural gas-based oxyfuels, NMEM = natural gas based membranes, and NGFC = natural gas (solid oxide) fuel cells.

One interesting observation is the performance of the petcoke IGCC with CCS study which although has an LCOE similar to its coal IGCC counterparts, the GHG emissions are lower [26]. This is largely due to the difference in indirect emissions from the fuel supply chain since petcoke is a waste product and no GHG emissions are attributed to its production. This difference in fuel supply chain emissions also partially explains why POXYD and POXY CCS have significantly lower emissions than their coal-based oxy-combustion counterparts. In fact, the POXY CCS case has near-zero lifecycle emissions for this reason, as nearly 100% of direct CO_2 produced is captured, and the impacts of indirect emissions are limited primarily to CO_2 in wastewater that we assumed to have ended up in the atmosphere which is relatively small over the life of the plant. The POXY CCS case has even lower emissions than the SOFC based power plants, which have the lowest known lifecycle CO_2 emissions of any coal or gas based power plant in the open literature. These SOFC plants often use a CO_2 capture strategy similar to the POXY CCS case (with nearly 100% capture of directly produced CO_2) but the other aspects of their life cycle, such as fuel production and transport, dominate their cradle-to-product GHG emissions.

Of course, the POXY CCS results depend on the common assumption that the O_2 content in the captured CO_2 stream does not prevent its sequestration, which is likely unrealistic. The POXYD point is therefore more realistic and yet has essentially the same cradle-to-product GHG emissions as SOFC-based systems. Although the LCOE is predicted to be higher than SOFC-based systems, SOFC-based systems for municipal power are not mature commercially and so the proposed POXYD process may be much more tractable in the nearer term. It is also important to note that most of the coal-based oxy-combustion processes the authors found in the literature and shown in Figure 5 did not report their captured CO_2 stream composition. For those that did, all except one of the coal-based oxy-combustion processes had high O_2 content in the captured CO_2. For those that did not, there was nothing in the design that was considered that would reduce the O_2 concentration, such as O_2 removal or by using O_2 deficient feeds that would result in complete O_2 consumption but incomplete combustion. Thus, the coal-based combustion points Figure 6 also contains the same unrealistic assumption that the captured CO_2 is sequesterable. Even in this case, POXYD—which meets pipeline specifications—has far less life cycle GHG emissions at essentially the same cost as its coal-based counterparts with their unrealistic and optimistic assumptions. To our knowledge, no studies on the additional cost and GHG impacts from implementing O_2 removal from captured CO_2 for coal-based oxy-combustion have been conducted and so we cannot compare POXYD to more realistic coal-based equivalents.

3.4 Cost of CO_2 avoided

The results of the CCA are shown in Table 7. The POXY (without CCS) case has no CCA listed, because the CO_2 emissions of this case are actually larger than the reference case, so the metric has no meaning. The results range from \$10 to \$42 (in 2016 USD) per tonne CO_2 avoided, depending on whether carbon taxes, transportation, and sequestration are considered. These metrics were computed using the LCOEs computed from Part I of this work [4] to which the reader is referred for information about how carbon taxes and CO_2 transportation and shipping (T&S) were computed.

Table 7: Summary of petcoke oxy-combustion system performance. See the supplementary material for additional details.

	Unit	POXY	POXY CCS	POXYD
CCS enabled		No	Yes	Yes
CCA without carbon tax and without T&S cost	\$/tonneCO_2eq	-	10.43	24.35
CCA without carbon tax and with T&S cost	\$/tonneCO_2eq	-	25.03	39.11
CCA with carbon tax and without T&S cost	\$/tonneCO_2eq	-	10.45	27.45
CCA with carbon tax and with T&S cost	\$/tonneCO_2eq	-	25.06	42.21

The CCA for the POXY design with CCS remained almost (additional \$0.02/tonneCO_2eq) unchanged when the carbon tax was taken into account, but increased by \$3.1/tonneCO_2eq for the POXYD design. This is because POXY CCS captured near 100% of direct emissions compared to POXYD. Although the CCA can increase to as much as \$25.06/tonneCO_2eq and \$42.22/tonneCO_2eq when the carbon tax and CO_2 T&S costs are considered, these figures are still lower than the benchmark \$50/tonneCO_2eq emissions tax primed to be imposed by government regulatory agencies. Ultimately, there is enough cost incentive to construct a new POXYD plant instead of constructing a new pulverized coal power plant under a \$50/tonne carbon tax policy. The LCOE vs CCA for POXY CCS and POXYD (CCA without carbon tax and without T&S cost metric) for various coal technologies exhibits a linear relationship, with the various technologies being clustered together as shown in Figure 6. Similarly, the petcoke oxy-combustion designs presented in this work followed the same trend, which shows good agreement in overall performance.

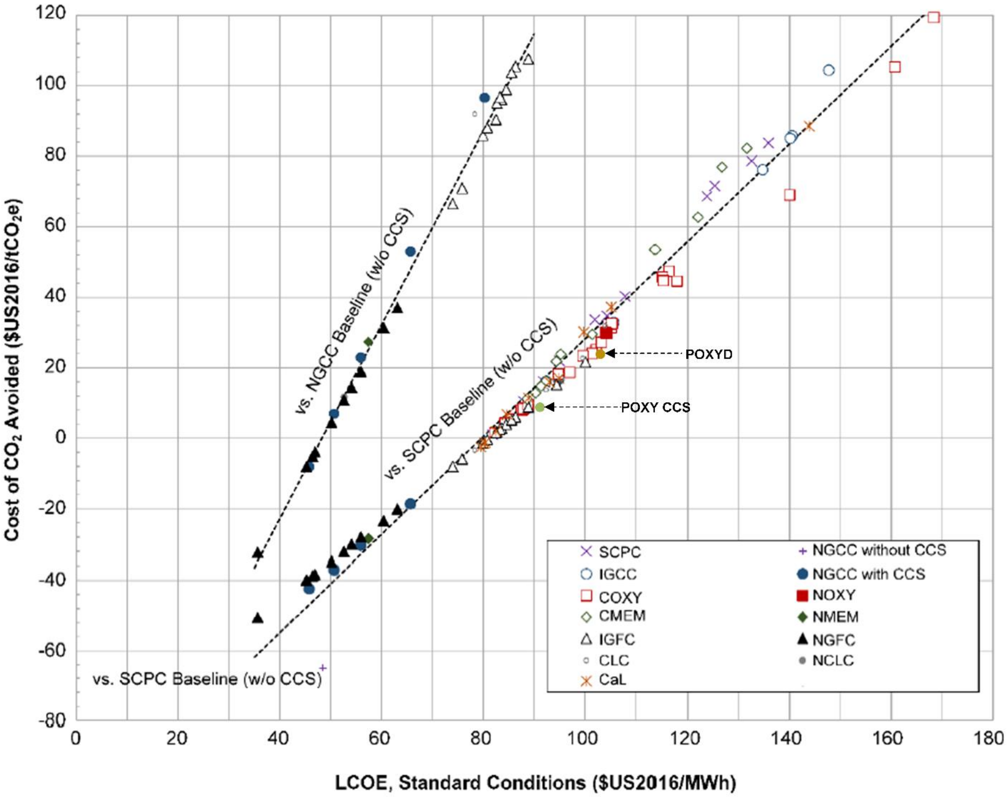

Figure 6: Scatter plot of LCOE vs. CCA calculated using the reference SCPC and NGCC plants without CCS. The plot depicts the comparative performances of the proposed petcoke oxy-combustion technologies and coal and natural gas power plants using various technologies. Adapted from Adams et al. [14] with data added from the present work. COXY = coal-based oxyfuels, CMEM = coal-based membranes, IGFC = integrated gasification (solid oxide) fuel cell, NGCC = natural gas combined cycle, NOXY = natural gas-based oxyfuels, NMEM = natural gas based membranes, and NGFC = natural gas (solid oxide) fuel cells.

3.5 Sensitivity analysis

A sensitivity analysis was conducted on the parameters that were used to compute the LCA and CCA (without carbon tax and without T&S cost) of the petcoke oxy-combustion designs in order to determine how these parameters affect the estimated environmental impacts and costs. We performed this analysis on the CCS enabled designs. The sensitivity analysis was conducted for the following parameters: petcoke emissions (0 to 5%), petcoke purchase price ($0/tonne to $50/tonne), rate of return (ROR) which was varied between 8% and 25%, CO_2 emission tax ($0/tonne to $80/tonne), and CO_2 transportation & storage (T&S) costs ($5/tonne to $15/tonne). When a parameter is varied, other parameters were kept constant in order to ascertain how the varied parameter impacts the overall impacts and CCA.

In this analysis, we assumed petcoke as waste; thus, no indirect emission on the use of petcoke as fuel. This assumption is completely reasonable given that petcoke is an unwanted product of crude oil refinery. Nevertheless, we have considered the allocation of some refinery emissions to petcoke as a future action when petcoke becomes desirable as a feedstock. Using a refinery product emissions allocation of 62% and 38% for diesel and gasoline products respectively from our prior work [27], up to 5% of the refinery emissions were allocated to petcoke to ascertain the impacts of petcoke indirect emission on the overall life cycle performance.

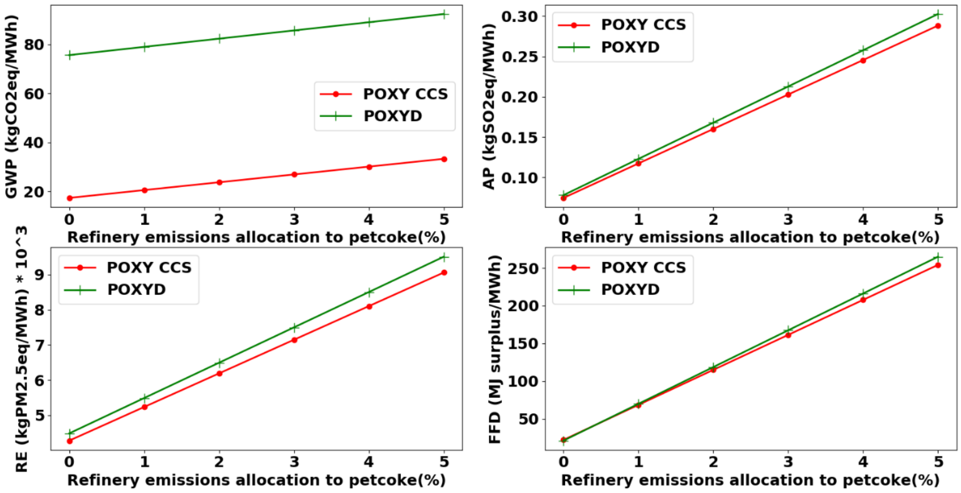

Figure 7: Effect of refinery emission allocation to petcoke on global warming potential, acidification potential, respiratory effects, and fossil fuel depletion using the CTCG analysis boundary

In Figure 7, the effect of petcoke emissions allocation on GWP is depicted. With an emission allocation of 5%, GHG emissions of 33.28 and 92.42 kgCO_2eq/MWh for POXY CCS and POXYD designs respectively were recorded which is still better than coal oxy-combustion (see figure 5). It should also be noted that those coal oxy-combustion studies did not consider the entire life cycle emissions which included pipeline transportation and fugitive CO_2 leaks. As depicted in Figure 7, the impact of emission allocation on AP, with a base case AP of 0.07 and 0.08 kgSO_2eq/MWh for POXY CCS and POXYD designs respectively, an increase to 0.29 and 0.30 kgSO_2eq/MWh resulted for a 5% refinery emission allocation. This is expected given the inherent emissions of the refinery operations. Even at that, this increase in AP is still lower than the AP of SCPC technology [15] which makes the petcoke oxy-combustion desirable. The effects of petcoke emission allocation were also explored on the life cycle respiratory effects of the petcoke oxy-combustion. A similar trend of an increase in emissions was observed as petcoke emissions allocation is increased to 5% as shown in Figure 7. The increase was up to 112 for both the POXY CCS and POXYD designs. Again, it is not surprising as refineries combust fossil fuels during operations emitting PM2.5 and SOx which are chemical stressors of particulate matter emissions. Allocating refinery emissions to petcoke implies that it is no longer a waste product of crude oil refining but rather a value-added product produced for other downstream purposes. Thus, an increase in fossil fuel depletion was observed as the refinery emission allocation percentage was increased. As illustrated in Figure 7, FFD increased from 22.1 to 254 MJ/MWh for the POXY CCS design and from 21.1 to 265 MJ/MWh for the POXYD design. Such an increase is due to the amount of petcoke consumed (up to 351 kg/MWh) which was assumed to have zero impact in the base case. This ultimately implies that petcoke is no longer a waste, but a value-added product produced from crude oil, which for now is not the case. Nevertheless, if it turns to be so, its FFD compares to that of the SCPC power plant.

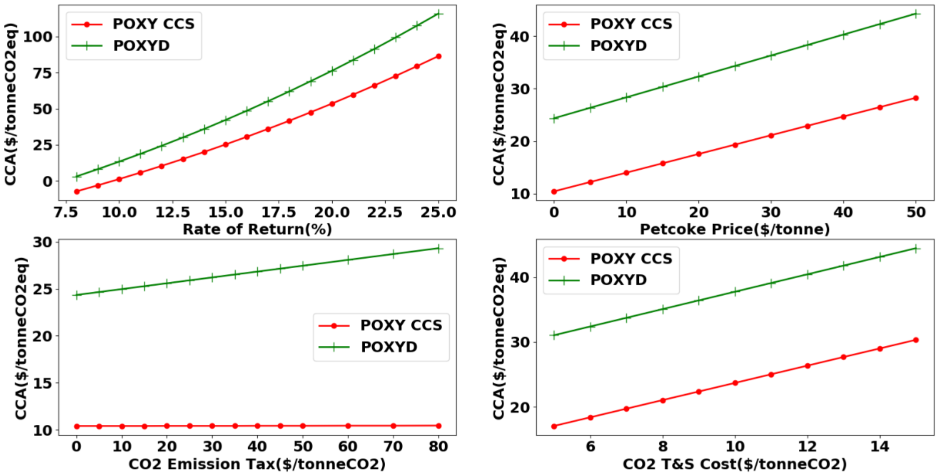

Figure 8: Effect of rate of return, petcoke price, CO$_2$ emission tax, and CO$_2$ T&S on the cost of CO$_2$ avoided (CCA)

Figure 8 shows the effect of the ROR parameter on the CCA. A negative CCA was observed at a ROR of 8% for the POXY CCS. This implies that even with CCS, the POXY CCS plant had lower LCOE compared to the reference plant. Thus, it indicates the plant is both cheaper and has lower GHG emissions than the reference case. Moving from a base case ROR of 12% to 25%, a CCA of \$86.42/tonneCO$_2$eq and \$115.9/tonneCO$_2$eq for the POXY CCS and POXYD designs respectively was recorded which is quite on the high side. But at a conservative ROR of 20%, a \$53.54/tonneCO$_2$eq and \$76.26/tonneCO$_2$eq for the POXY CCS and POXYD designs respectively are quite feasible. Also Figure 8 depicts how shifting from a petcoke price of \$0/tonne affects the CCA. At worst-case scenario when petcoke sells at \$50/tonne, the CCA for the POXY CCS and POXYD designs are \$28.24/tonneCO$_2$eq and \$44.26/tonneCO$_2$eq respectively which is still competitive compared to the \$50/tonneCO$_2$eq carbon tax. Even with carbon tax implemented in the plant at a cost as high as \$80/tonneCO$_2$eq, the CCA was as low as \$10.47/tonneCO$_2$eq (slope of 0) and \$29.31/tonneCO$_2$eq for the POXY CCS and POXYD designs respectively as illustrated in Figure 8. This is due to the high direct CO$_2$ capture rate of the oxy-combustion technology where most of the emissions are indirect emissions that are not captured. Considering the effect of CO$_2$ T&S cost on CCA, an increase of \$1.33/tonneCO$_2$eq and \$1.34/tonneCO$_2$eq in CCA occurs for every change in CO$_2$ T&S cost for POXY CCS and POXYD designs respectively. In Figure 8, moving from a base case CO_2 T&S cost of \$11/tonneCO_2 to \$15/tonneCO_2 which corresponds to a 36% increase, the CCA for the POXY CCS and POXYD designs increased to \$30.34/tonneCO_2eq and \$44.47/tonneCO_2eq respectively. When this is compared to the CCA shown in figure 6, the performance of the petcoke oxy-combustion designs is still viable.

4. Conclusions

In this study, the LCA and CCA of a petcoke oxy-combustion technology were presented in order to determine its potentials as an avenue for disposing of the ever-increasing stockpiles of petcoke. This study was based on the design and economics of three petcoke oxy-combustion power plants namely - petcoke oxy-combustion without carbon capture and sequestration (CCS), petcoke oxy-combustion with CCS, and petcoke oxy-combustion with CO_2 purification by distillation and CCS presented in part I of this work. The LCA scope covered in this work included the direct and indirect material and energy input to the designs with their corresponding emissions to the environment for a 1MWh of electricity delivered. While TRACI 2.1 was used to quantify the impacts of each design at the midpoint level, ReCiPe 2016 was used to calculate the impacts at both midpoint and endpoint levels of each design.

It was found that the design without CCS had a high life cycle GWP of 1089 kgCO2eq/MWh compared to the POXY CCS and POXYD designs with life cycle GWP of 17.32 kgCO2eq/MWh and 75.65 kgCO2eq/MWh respectively. Interesting observations were the high AP and RE for the POXY design using TRACI 2.1 (or FPMF and TA respectively for the ReCiPe 2016) due to the release of SO_2 to the environment. Unlike the POXY design, the SO_2 in the POXY CCS and POXYD designs ended up in the pipeline for which we assumed does not compromise its integrity. Other than that, the effect of CCS technology was seen in other impacts as the POXY CCS and POXYD designs had higher impacts compared to the POXY.

We considered both POXY CCS and POXYD in this work to drive home the extra energy and environmental effects caused in order to purity the captured CO_2 which other oxy-combustion studies did not consider. Our results showed that POXYD had higher impacts due to the trade-off between capture rate and energy penalty in the distillation operation of CO_2 separation leading to a 95% capture rate compared to the POXY CCS design which had near 100% capture.

Nevertheless, the high amount of CO_2 captured constituted its portion of emission with regards to pipeline construction to transport the CO_2 to the sequestration site. Overall, when both POXY CCS and POXYD designs were compared to the petcoke IGCC, coal IGCC, and SCPC power plants, their emissions were lower even when the indirect petcoke emissions were considered via sensitivity analysis.

Likewise, the CCA of both POXY CCS and POXYD was compared to that of the start-of-the-art coal-fired power plants. With a base case LCOE, the cost of CO_2 avoided (CCA) for the POXY CCS and POXYD designs were \$10.43/tonneCO_2eq and \$24.35/tonneCO_2eq respectively. Even when the cost parameters were varied at the worst-case scenario, the highest CCA observed was \$115.9/tonneCO_2eq for the POXYD design. Finally, we can conclude that petcoke oxy-combustion for power generation has a future as a viable means of petcoke disposal. Notably, POXYD design is the design of choice even though it has high emissions and costs which are the trade-offs to meet the CO_2 pipeline standard.

Nomenclature

Abbreviations

AP	Acidification potential
CAPEX	Capital expenditure
CCA	Cost of CO_2 avoided
CCS	Carbon capture and storage
CP	Carcinogenic potential
CTPG	Cradle-to-plant-exit gate
CTCG	Cradle-to-customer gate
ED	Ecosystem diversity
EP	Eutrophication potential
ETP	Ecotoxicity potential

FFD	Fossil fuel depletion
FPMF	Fine particulate matter formation
FT	Fischer-Tropsch
FWET	Freshwater ecotoxicity
FRS	Fossil resources scarcity
GHG	Greenhouse gas
GWP	Global warming potential
HCT	Human carcinogenic toxicity
HEN	Heat exchanger network
HH	Human health
HNCT	Human non-carcinogenic toxicity
LCA	Life cycle assessment
ME	Marine Eutrophication
MDSP	Minimum diesel selling price
MDEA	Methyl di-ethanolamine
NCP	Non-carcinogenic potential
ODP	Ozone depletion potential
OPEX	Operating expenditure
POXY	Petcoke oxy-combustion
POXY CCS	Petcoke oxy-combustion with CCS
POXYD	Petcoke oxy-combustion with CO_2 purification by distillation and CCS
RA	Resource availability
RE	Respiratory effects

ROR	Rate of return
SF	Smog formation
SOD	Stratospheric Ozone depletion
TET	Terrestrial ecotoxicity
WC	Water consumption

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Chapter 7

Conclusions and Future Work

7.1 Conclusions

The focus of this thesis has been on exploring pathways by which the "end-of-life" of the ever-growing amount of petcoke stockpile can be disposed of in the most cost-effective and environmentally friendly way. Thus, this work sought to find feasibile technology and design configurations by which petcoke can be disposed with economics and environmental impacts as criteria. Specially, petcoke disposal via liquid fuels production and electricity generation were investigated of which the outcome has been promising. Instead of stockpiling petcoke, there are economic and environmental benefits of either converting petcoke for transportation fuel production and/or for electricity generation. While the former can be feasible in Ontario province of Canada, the later is needed in the high carbon-intensive electricity grid emission province of Alberta. Based on our findings in this study, the following primary conclusions are made:

- Petroleum coke gasification that integrates natural gas reforming within the gasification steps is recommended for liquid fuels production as it is financially, technologically, and environmentally more feasible than the other petcoke to liquids design strategies. Our results of this design and analysis have shown improved performance in terms of carbon conversion efficiency, energy efficiency, minimum diesel selling price, net present value, and cradle to grave environmental impacts when compared to the conventional crude oil and the Canadian oil sands derived diesel. Thus, it is the technology to adopt for the future of petroleum conversion to liquid fuels.

- Developing a waste-to-energy facility running on petcoke is recommended as it will offset some amount of emissions emanating from the traditional extraction of fossil energy sources. This is based on the finding from our novel environmental impact assessment of petcoke and/or natural gas to transportation diesel which showed a system with minimal harm to the environment when compared to the status quo processes. Therefore, as the world is advocating for proceeses with little or no footprints, petcoke should be considered in a waste-to-energy facility.

- To dispose the stockpiled petcoke via electricity generation, oxy-combustion technology is recommended as the most feasible option for the two petcoke to electricity pathways considered. One inherent advantage of the oxy-combustion technology is its flue gas size and low-energy intensive CO_2 separation via flash separation. Also, based on coal-based studies, it is evident that the oxy-combustion technology is superior to the traditional coal-fired combustion and thus will require an air separation unit which will provide the oxygen needed to operate the oxy-combustion power plant. When operating an oxy-combustion power plant, despite the presence of a high concentration of O_2 in the captured CO_2 stream alongside the efficiency loss during the purification of the CO_2 stream, the net efficiency of the petcoke oxy-combustion is still competitive when compared to the status quo. Integrating this technology into the electricity grid in a province such as Alberta with high-carbon intensive grid emissions, the GHG emissions from the power sector can be reduced by up to 50% with reductions in other environmental impacts such as eutrophication, respiratory effects, ozone depletion, smog formation, etc.

- It is evident that the petcoke oxy-combustion power plant outperformed the petcoke IGCC power plant. Nevertheless, where a gasifier (say, coal gasifier) is already in place, petcoke conversion to electricity via the integrated gasification combined cycle (IGCC) has proved to be another viable alternative to petcoke disposal. Given that petcoke is a waste, there are economic and environmental incentives to use petcoke to displace coal as fuel in the IGCC power plants. Hence, instead of decommissioning the existing coal IGCC power plant, logistics that can channel the produced petcoke (rather than stockpiling) to the IGCC plant is all that is needed.

7.2 Future Work

Despite the promising results achieved in this study that explored the conversion of petcoke to fuels and electricity paving ways for possible future commercializing of the proposed petcoke conversion pathways, there are still some limitations in this work which needs to be explored which the results of the analysis can help to enhance the conclusions made in this study. Based on the studies and analysis carried out throughout this thesis, the following areas are highlighted which requires further investigation:

- **Effects of petcoke stockpiling:** Integrating the environmental effects of petcoke stockpile in the overall analysis would have improved its robustness. This would have allowed critical questions as to whether petcoke should actually be stockpiled indefinitely or converted to either fuels, chemicals, or electricity to be addressed. Unfortunately, in the literature, there are lack of data that provides a comprehensive information on the effects of petcoke stockpiling. To such effect, new analysis that involves field trip to petcoke stockpile site, laboratory sampling of petcoke, survey of persons living in the neighbourhood of a petcoke stockpile, and water, air, and soil sampling are required. Does petcoke leach into groundwater?, how does it affect the respiratory system of residents?, and to what extent does all these side effects take place? These are questions that needs to be addressed for which the answer would determine whether or not the pathways proposed in this thesis should actually be pursued.
- **Startup and operability of petcoke gasifier:** Prior to the commercialization or adoption of the proposed petcoke to liquids and even the petcoke IGCC technology, studies that evaluate the startup and operability of the gasifier is required. It is known that the operation of a gasifier is quite

challenging given the intermittent failure of the unit. To overcome this issue, gasifiers are usually operated in parallel, usually for backup purposes. This amounts to a huge capital investment leading to a longer payback period or at least a higher product selling price to recuperate investment. Similar to the start-up study for a coal based gasifier (Ghouse et al. 2017), an optimal operating trajectory of the petcoke gasifier via a detailed startup and operability analysis would help in the efficient running of the gasifier which will in turn help in the overall profitability and emission reduction of the overall system.

- **Alternative source of hydrogen production:** Similarly, the petcoke gasifier integrated with natural gas reforming proposed in this work can be adopted as a novel pathway for other chemical production. By adjusting the steam to carbon ratio, hydrogen-rich syngas with a H_2/CO ratio of up to 6 can be produced making it a viable source of hydrogen production. Holistically, it will serve multiple purposes of disposing (or reducing) the stockpiled petcoke as some amount of natural gas consumed per kg of syngas produced is reduced; thus, minimizing the environmental impacts of natural gas extracting and transportation. But to confirm those claims, the design and feasibilty study of the petcoke to hydrogen needs to be carried out.

- **Optimal design under uncertainty of the proposed designs:** We have used constant operating parameters during the modeling and simulations carried out in this thesis which has performed at its optimal conditions. However, this is usually not the case in chemical systems as parameters tend to deviate from design set points during operations. Also, petcoke used in the study was considered to be of uniform composition without considering the effects of differences in petcoke composition delivered from different refinery. In the cost analysis, the effects of market uncertain were not considered given the variation in demand due to seasonal differences. Thus, it is recommended that a study that incorporates design under uncertainty needs to be carried out in order to ascertain the performance of the systems at the realization of uncertainty in the parameters used in the system analysis.

- **Optimization of a polygeneration system:** In addition to the optimal design under uncertainty, expanding the product portfolio to include the production of hydrogen, methanol, dimethyl ether, etc. might further improve the performance of the proposed petcoke conversion processes. Also, as Canada has high amount of forestry products, the use of biomass or other biological wastes such as municipal solid waste, agricultural and household waste, industrial wastewater, etc as feedstock in addition to petcoke and natural gas proposed in the work might prove to be more beneficial. This will require the use of anaerobic digester to convert the wastes to biogas which is biogenic source of methane. Overall, the performance of a petcoke plant that has a combination of anaerobic digester, gasifier, and oxy-combustor units that can switch feedstock types and product portfolios needs to be investigated. This will require the formulation of a mixed integer non-linear programming optimization model which can be solved to global optimal solution using the commercial solver or new alternative decomposition strategies.

7.3 Clarifications

In this thesis, the terms internal rate of return (IRR) and equity rate of return (ROR) were used interchangeably for discounting the annual cash income in order to account for the time value of money. This is to provide clarifications that the formulation and usage are the same and does not change the analysis and the subsequent results.

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