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Supply Chain Optimization of Flare-Gas-To-Butanol Processes in Alberta

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ABSTRACT

In this work, the economic feasibility of combining a novel portable gas-to-methanol process with a novel methanol-to-butanol process is examined. The gas-to-methanol process converts waste flare gas into methanol using a series of truck-mounted devices deployed at oil production wellheads. The methanol-to-butanol process uses a new proprietary catalyst which produces butanol via a diketene intermediate at a large centralized facility. The goal of this work is to identify the best ways of commercializing this technology in Alberta. To do this, a supply chain optimization model is formulated which considers specifically how many gas-to-methanol trucks should be used and where specifically in Alberta they should be deployed, the specific suppliers of CO_2 to use, where the location of the central methanol-to-butanol facility should be located, and the costs of transportation of materials between locations. The model framework also considers the possibility of getting methanol in full or in part by alternative means such as producing methanol from conventional pipeline natural gas, or purchasing methanol from petrochemical or biomass-based routes. The supply chain optimization problem is formulated as an NLP and BARON is used in a Pareto analysis considering weighted combinations of economic and environmental objective functions. The resulting analysis provides a variety of possible viable strategies which can provide both profitability and reduced environmental emissions in Alberta by using a combination of the novel portable flare gas capture devices with more conventional gas-to-liquids technologies.

Key words: Supply chain optimization, Sustainability, Portable technology

INTRODUCTION

In Canada, around 2.5 billion cubic meters of natural gas are flared every year, according to estimates from satellite data.[1] Typically, this “flare gas” is a waste product of oil or gas production (such as associated gases) which is too expensive, difficult, or costly to capture for sale or use. As a result, gas flaring causes significant GHG emissions. However, if the flare gas could be recovered efficiently and cost effectively, this could not only avoid wasting a non-renewable energy source but also contribute significantly to greenhouse gas (GHG) reduction.[2]

To harness the high potential for flare gas capture, the key problems which restrict flare gas recovering and processing must be overcome. Flare gas sources are geographically dispersed and generally contain small quantities in most of the sources. For example, in Alberta, meaningful amounts of flare gas are produced at locations covering over 1000 different townships.[3] Due to high costs associated with flare gas recovering and purification, it is not economical to recover low quantity flare gas sources using existing technologies. One solution for this problem is to use mobile technology which converts flare gas to some useful products at the flare gas site. Pioneer Energy, Inc.[1] is currently developing two truck-mounted devices called the Mobile Alkane Gas Separator (MAGS) and the Portable Enhanced Recovery Technology-2 (PERT-2), which can each be driven to a remote flare gas site and used to convert flare gas to methane (via MAGS) and then methane to methanol (via PERT-2).[4] The methanol can either be consumed locally as a fuel or trucked away from the flare gas site for sale to the market. However, the profitability of the MAGS/PERT-2 process by itself may be limited, due in part to the relatively low price of methanol. However, Pioneer Energy is also developing a new catalyst and associated catalytic process which converts methanol to butanol,[5] which is worth about four times the price as methanol (weight basis). If the methanol is trucked to a central facility where it is converted to butanol via a centralized process, then the profitability may be significantly higher, making flare gas capture much more attractive and commercializable.

This study probes the best way to use Pioneer Energy's technologies in Alberta such that the process is both profitable and reduces GHG emissions. In order to understand how Pioneer Energy should apply this technology, the entire supply chain must be examined. The key unknowns of the process are: the best flare gas sites to use and the quantity of used flare gas at each; which CO_2 supplier(s) should be used and how much should be purchased from each; and the best geographical location and capacity of the central methanol-to-butanol facility. The mobile flare gas capture technology was also compared to alternatives that do not use flare gas such as purchasing conventional natural gas to produce methanol using conventional gas-to-methanol methods, or directly purchasing methanol or bio-methanol from suppliers in Alberta. This is very important because the best option may not necessarily use the MAGS or PERT-2 devices.

[1] Disambiguation: Pioneer Energy in this paper refers to the U.S.-based energy technology company, not the Ontario-based automotive fuel service station company with the same name.

Supply chain optimization for the chemical process industry is an area of active research (see [6, 7] for reviews on the topic). One of the most important challenges in supply chain optimization is the development of an appropriate process model.[8] Often, constructing rigorous models for chemical engineering applications such as the planning and scheduling of manufacturing facilities leads to a mixed-integer nonlinear programming (MINLP) problem formulation, where process flow variables specified in the form of continuous variables and sequencing decision variables could be specified in the form of integer variables. Existing methods to solve MINLP optimization problems (such as various forms of branch and bound, outer approximation, and generalized Benders decomposition methods) are generally suitable only for small-to-medium size problems because the computational requirement grows exponentially as the number of variables increase.[8] Thus, when it is possible, converting the MINLP problem into a problem that is easier to solve can potentially reduce computation times. For instance, Bournazou et al. transformed an MINLP optimization problem in to an NLP problem to find optimal aeration profile for sequencing batch reactors and have shown that the proposed model is accurate and remarkably fast.[9] Also, Capitanescu et al. proposed an NLP formulation for the MINLP problem of optimal power flow, by reformulating an MINLP problem as a mathematical programming with equilibrium constraints (MPEC) problem.[10] In addition, Schmidt presented a detailed reformulation of a class of large scale MINLP problems into NLP problems and successfully applied that for an optimization problem in real-world gas networks.[11]

Therefore the objective of this work is to develop a supply chain model and associated optimization framework which considers the all potential supply chains for this process. The model considers the economic factors such as transportation distances, market prices, flare gas locations and capacities, supplier locations and capacities, access to natural gas pipelines, net present value computations, and CO_2 emissions avoided in order to create a Pareto optimum curve balancing profitability with GHG reduction. An NLP formulation was used to reduce computation time and retain the nonlinear characteristics of the model. The results of the study are used to help understand which technologies should be developed.

MODEL FRAMEWORK

A sketch of the supply chain superstructure used in the model is shown in Figure 1 and described in the following sections. The superstructure represents all possible supply chain routes considered in the model. Note that all dollar amounts in this report refer to US Dollars. The conversion rate used in this analysis is 1 USD=1.15 CAD.

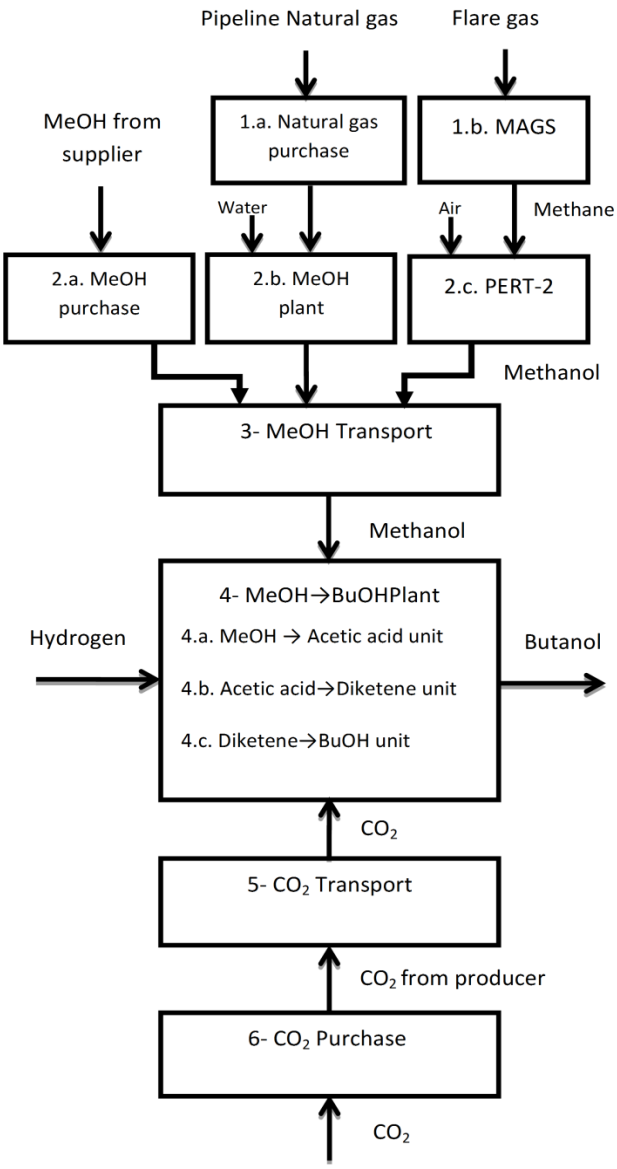

Figure 1. Model framework

Conventional Natural Gas-To-Methanol Plant

These subsystems consider the option of purchasing natural gas directly from conventional natural gas pipelines and using it to produce methanol via a traditional gas-to-methanol process. As shown in Table 1, the location of the gas-to-methanol facility (if it exists) is a decision

variable selected by the optimization algorithm, represented by its latitude (p_{2x}) and longitude (p_{2y}) coordinates. The location is permitted to be anywhere within the Alberta province.

Natural gas purchasing (subsystem 1.a)

Natural gas which has been purchased from the pipeline has to be transported to the gas-to-methanol plant site. For this study, two main natural gas pipeline routes in Alberta, the ATCO and NGTL pipelines, are considered. Theoretically, any point on these pipelines could be a potential connection point at which natural gas could be withdrawn. However, using published maps of the natural gas pipelines,[12] 100 discrete locations were manually selected as potential locations for a pipeline connection considered in the model. The locations were chosen at pipeline junctions or spur termini where access to pipelines is expected to be the easiest. The locations were also spaced out roughly equidistant from each other, but with higher densities near major urban areas. The decision variables for this step are the amounts of gas purchased from each of these 100 nodes, namely $n_{g1} \dots n_{g100}$. It is assumed that price of the natural gas purchased at these connection points are the same, as given in Table 5.[13] Note that if the optimizer may select a condition where no natural gas is purchased from pipelines, meaning that all $n_{g1} \dots n_{g100}$ are zero. In addition, constraints are added such that the total amount of gas purchased from the ATCO and NGTL pipeline systems are no more than 5% of the current capacity.

Table 1. The 194 decision variables of the optimization problem

Decision variables	Description
x_1	Plant capacity *(tonne/yr)*
$n_{g1} \dots n_{g100}$	Amount of purchased natural gas from pipelines at each of the 100 possible access points, *(tonne/yr)* (Subsystem1.a)
$n_{f1} \dots n_{f76}$	Amount of captured flare gas used from each of the 76 sites considered, *(tonne/yr)* (Subsystems1.b and 1.c)
$n_{m1} \dots n_{m4}$	Amount of methanol purchased from sources 1-4, *(tonne/yr)* (Subsystem2.a)
$n_{c1} \dots n_{c8}$	Amount of purchased CO_2 from each of the 8 sites, *(tonne/yr)* (Subsystem6)
(p_x, p_y)	Methanol-to-Butanol plant location latitude and longitude, (DD) (Subsystem4)
(p_{2x}, p_{2y})	Gas-to-Methanol plant location latitude and longitude, (DD) (subsystem2.b)

It is also assumed that a pipeline spur will be built between any pipeline connection location and the selected gas-to-methanol plant location. The cost of building pipelines used in the model is $0.57250 \frac{\$}{km\left(\frac{tonne\ shipped}{yr}\right)}$ based on the real costs of previously constructed Canadian pipelines.[14] Therefore, the model considers the capital cost of pipeline construction as a linear function of the

Euclidian distance, D, between the pipeline connection and the gas-to-methanol plant, and the capacity. In this study, the distance is computed as follows

$$D = Earth\ mean\ radius\ (km) \times \sqrt{(\Delta x^2 + \Delta y^2)} \quad (1)$$

Where Δx and Δy are the longitudes and latitudes differences between the source and gas-to-methanol plant location, in radians.

Gas-to-methanol plant (subsystem 2.b)
The overall reaction of the gas-to-methanol production process is given by following equation:

$$CH_4 + H_2O \rightarrow CH_3OH + H_2 \quad (2)$$

The conversion ratio of this process (the mass of methanol produced divided by the mass of methane consumed), represented by $r_{2.b}$, is derived from a source which reported that 32 GJ of natural gas is required per 1 tonne of methanol produced for the traditional gas-to-methanol process.[15] Factoring in the minimum lower heating value (LHV) of TransCanada natural gas,[16] this translates to $r_{2.b}$= 1.5722.

The fixed capital investment (FCI) of the gas-to-methanol plant is estimated based on the six-tenths rule,[17] as given by Equation (3). According to,[17] a gas-to-methanol plant producing 55 thousand tonne/yr of methanol cost about $15 million to construct in the year 2000. This is converted into 2015 dollars by using the Chemical Engineering Plant Cost Index (CEPCI), which is given in Table 2.

$$FCI = \frac{575}{394.4} \times \$15 \times 10^6 \times \left(\frac{MeOH_{cap}}{0.055\ Mtonne/yr}\right)^{0.6} \quad (3)$$

where $MeOH_{cap}$ is the methanol production capacity and given by

$$MeOH_{cap} = r_{2.b} \times \sum_i n_{gi} \quad (4)$$

Table 2. General economic data used for the economic analysis in this work

Parameter	Value
Working days in a year	330 day/yr
Chemical engineering plant Cost index for 1990[18]	360
Chemical engineering plant Cost index for 2000[18]	394.1
Chemical engineering plant Cost index for 2014[19]	575
Plant life time	30 years

Therefore the total capital cost of step 2.b is the sum of Equations (3) and (4).

The operating costs (not related to raw consumables) are estimated using the following heuristics that estimate various aspects of the operating costs as a function of the capital cost and the operating labour.[20] These details are summarized in Table 3. The operating labour (not including overhead) can be estimated simply by using the number of operators on duty at any given time and their wages paid; the average wage in Alberta for typical industrial and manufacturing engineers[21] is CAD 40.92/hr (or $US 35.5826/hr), which was used in this analysis. Chauvel and Lefebvre[15] have reported that 7 operators per shift are required for a methanol plant with production capacity of 1,800 tonne/day. At larger capacities, the number of operators required grows slowly, with a power law exponent 0.2.[17] Then, the operating labour cost (OPL) of the process will be estimated as Equation (5):

$$OPL\left(\frac{\$}{yr}\right) = operators\ per\ shift \times 5(shifts) \times 2080(hr/yr\_operator) \times wages(\frac{\$}{hr}) \times (\frac{MeOH_{cap}}{1800\ tonne/day})^{0.2} \quad (5)$$

Table 3. Gas-to-methanol plant costs

	Plant Costs/income component	Estimated cost/income
1	Total capital investment ($)	Fixed capital investment/0.85
2	Working capital investment ($)	Total capital investment – fixed capital investment
3	Operating labour cost ($/year)	Equation (5)
4	Operating supervision($/year)	0.15×operating labour
5	Utilities($/year)	0.1×revenue if sold
6	Maintenance and repairs($/year)	0.07× fixed capital investment
7	Operating supplies ($/year)	0.15×maintenance and repairs
8	Laboratory Charges ($/year)	0.15×operating labour
9	Patents and Royalties($/year)	0.01×fixed capital investment
10	Catalysts and Solvents($/year)	0.01×fixed capital investment
11	Direct Production Costs($/year)	Sum of 3 to 10+ raw materials
12	Insurance($/year)	0.01×fixed capital investment
13	Local taxes($/year)	0.02×fixed capital investment
14	Rent($/year)	0
15	Fixed Charges($/year)	Sum of lines 12 to 14
16	Plant Overhead Costs($/year)	0.6×(operating labour + operating supervision + maintenance &repairs)
17	Manufacturing Costs($/year)	Direct Production Costs+ Fixed Charges+ Plant Overhead Costs
18	Administrative Costs($/year)	0.15×(operating labour + operating supervision + maintenance and repairs)
19	Distribution and Selling Costs($/year)	0
20	Research and Development($/year)	0
21	General Expenses ($/year)	Administrative Costs+ Distribution and Selling Costs+ Research and Development

22	Total Production cost($/year)	Manufacturing Costs + General Expenses

The utility cost of many chemical plants is approximately in the range of 5-10% of product sales.[20] Therefore, a 10% of product sales approximation is used in the model. It should be noted that methanol is not actually sold in the model because it is consumed in the methanol-to-butanol process and its price is only used to estimate the utility cost of the process.

The remaining plant costs are described briefly in Table 3, and are based on common heuristics.[20]

2.2 Methanol production using MAGS and PERT-2 (subsystems 1.b and 2.c)

The optimization algorithm considers the option of using the MAGS/PERT-2 systems at flare gas sites across Alberta as shown in Figure 2. This figure is reproduced from an annual report by Alberta Energy Resources.[3] Different colors show different flaring amounts grouped by township. For this study, only flare sources with capacity of equal or greater than 30% of the capacity of one PERT-2 unit (3135 tonne/yr) are considered in the model as potential flare gas sources. This is because it is assumed that a PERT-2 unit would not be purchased if it would be used at below 30% of its capacity of 500 mcf/day. As a result, the 20 red sites and 56 yellow townships were considered in the analysis as potential flare gas sources. This is represented in the model as 76 decision variables $n_{f1} \dots n_{f76}$ representing the amount of flare gas captured from each of the 76 locations. The amount of available flare gas is limited,[3] therefore the variables are constrained to maximum values equal to the available flare gas at each source.

Based on Pioneer Energy's internal studies, MAGS recovers 2/3 of the flare gas as methane (on a weight basis). In addition, the net revenue of MAGS is approximately the same as its total operating cost; this means that the net cost of producing methane from flare gas (including the cost of the flare gas) is effectively zero.

PERT-2 produces methanol by a different route than the traditional gas-to-methanol process, with about 80% conversion of methane into methanol via the net reaction:[4]

$$6\,CH_4 + 4\,H_2O + 3\,O_2 \rightarrow 4\,CO_2 + 2\,CH_3OH + 12\,H_2 \qquad (6)$$

The CO_2 produced is captured at high purity and sold on site (for use in enhanced oil recovery) along with electricity produced by the combustion of the H_2 and unconverted methane in a combustion microturbine. Key parameter and cost data for PERT-2, which are based on Pioneer

Energy's internal research, are shown in Table 4. Note that it is assumed in the model that PERT-2 units are purchased in integer amounts, so even if only a small amount of flare gas is selected by the optimizer, one PERT-2 truck will still be required.

Table 4. Cost parameters of PERT-2 as estimated by Pioneer Energy

Parameters of PERT-2	Value	Unit	Alt. Value	Alt Unit
Capacity of one PERT-2 subsystem	500	mcf/day	9.5	tonne CH_4/day
Operating labour of one PERT-2 subsystem	400	$/day	42.1053	$/tonne methane
Operating costs of one PERT-2 subsystem	2950	$/day	310.5263	$/tonne methane
Capital costs of one PERT-2 subsystem	3	$million	3.45	$ million (CAD)
Selling price of electricity of one PERT-2 subsystem	1000	$/day	105.2632	$/tonne methane
Selling price of CO_2	39	$/tonne CO_2	71.3271	$/tonne methane
Working days in a year	330	day/yr	-	
Net reaction conversion	80	%	-	

Direct Methanol Purchasing (Subsystem 2.a)

For comparison purposes, direct methanol purchasing from the open market is considered as the third means of procuring methanol. In this case, the optimization algorithm may decide the amount of methanol purchased from any of the four major suppliers in Alberta considered in the analysis. Although the prices for each are assumed to be the same,[22] as shown in Table 5, and they have different locations as shown in Figure 2 and different capacity limits. One of these sources produces methanol from municipal bio-waste which is treated separately because it can be considered to have approximately zero net CO_2 emissions per tonne of methanol produced. Though this does not affect the economics, this is relevant when CO_2 emissions are taken into account as discussed in section 4.

Table 5. Price of chemicals

Chemical	Price
Natural gas[23]	$184/tonne
Water[20]	$19.1/tonne
Hydrogen[24]	$3080/tonne
Methanol[22]	$499/tonne
n-Butanol[25]	$2000/tonne
CO_2 selling price[26]	$27/tonne
Acetic acid[27]	$670/tonne
CO_2 purchase price[26]	Variable between $30-40/tonne

Methanol Transport (Subsystem 3)

In this work, it is assumed that methanol is transported by train from the point of purchase or production to the location of the methanol-to-butanol facility. The shipping rates are assumed to be the same, regardless of its source. The distance between the point of purchase and methanol-to-butanol central facility is computed using the Euclidian distance between two points. Transportation fees are derived from the recent cargo fees posted by Canadian National. The price of year 2014 for the transport of chemical products (including methanol) from Calgary to Edmonton is $2904/car (CAD 3339/car). Based on the average weight of a chemical train car, (90 tonne) and the known distance between those cities (304 km), the cost per tonne-km shipped of methanol is estimated to be $0.1061 per tonne per km.[28]

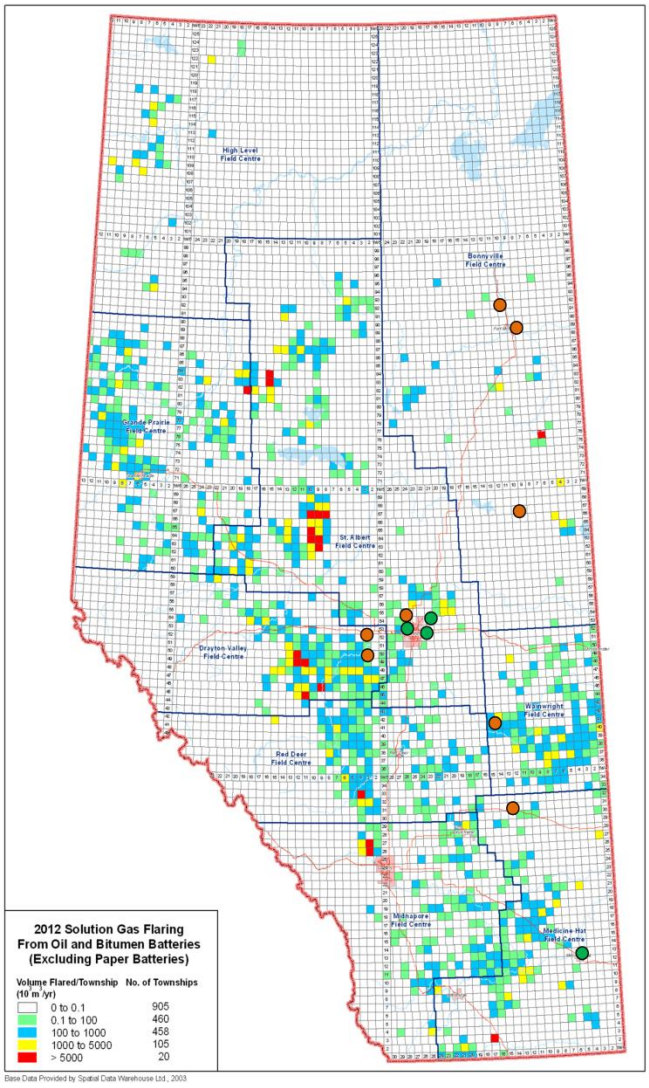

Figure 2. Alberta flare sites map reproduced from;[3] Orange and green circles on the map show selected CO_2 sources and methanol suppliers, respectively.

Methanol-To-Butanol Process (Subsystem 4)

Pioneer Energy has developed a new catalytic route for producing butanol from methanol, CO_2, and H_2. The overall route reaction is given by Equation (7)

$$2CH_3OH + 2CO_2 + 6H_2 \rightarrow C_4H_9OH + 5H_2O, \text{ total conversion of methanol} \approx 80\% \quad (7)$$

The individual reactions which comprise this route are as follows

$$2CO_2 + 2H_2 \rightarrow 2CO + 2H_2O, \text{ (conversion=100\%,[29])} \quad (8)$$

$$2CH_3OH + 2CO \rightarrow 2CH_3COOH, \text{ (conversion of methanol=90\%,[15])} \quad (9)$$

$$2CH_3COOH \rightarrow 2C_2H_2O + 2H_2O, \text{ (conversion=90\%,[15])} \quad (10)$$

$$2C_2H_2O \rightarrow C_4H_4O_2, \text{ (conversion=100\%,[30])} \quad (11)$$

$$C_4H_4O_2 + 4H_2 \rightarrow C_4H_9OH + H_2O, \text{ (conversion=100\%,[5])} \quad (12)$$

The conversion ratios can be estimated based on Equation (7):

$$r_4 = \frac{tonnes\ of\ butanol}{tonnes\ of\ methanol} = \frac{1}{2} \times \frac{Mw_{BuOH}}{Mw_{MeOH}} \times conversion = 0.92528 \quad (13)$$

To estimate the costs of the main plant, the costs of its individual subsystems were considered. The plant includes three major sub subsystems: 4.a. MeOH to Acetic acid subsystem, 4.b. Acetic acid to Diketene subsystem and 4.c. Diketene to BuOH subsystem. To estimate the costs of the subsystems, it is assumed that each are located in the same facility.

Subsystem 4.a: methanol to acetic acid

Acetic acid is produced by the carbonylation of methanol according to Equation (9) and the required CO is produced from a reverse water gas shift reaction (Equation (8)). Timmerhaus et al.[17] suggest a power law relationship for the prediction of capital cost of plants of this type. After adding CEPCI indices to convert the predicted cost into 2014 dollars, the capital cost equation used in the model becomes

$$FCI\ (\$) = \left(\frac{575}{360}\right) \times \$1.2216 \times 10^4 \times Ac_{cap}{}^{0.68} \quad (14)$$

Where Ac_{cap} is the acetic acid produced in tonnes/year and calculated using Equation (9) with conversion of 90% as follows:

$$Ac_{cap} = conversion \times \frac{60.05}{32.04} \times tonnes\ per\ year\ of\ total\ methanol \quad (15)$$

To estimate the operating costs of the acetic acid plant, the operating labour cost can be used as a basis. BASF operates an acetic acid plant with 4 operators/shift and production capacity of 80,000 tonne/yr,[15] and so this information was used in the model to predict the operating labour cost according to Equation (5). Using the same approach, the utility costs are approximated to be 10% of the revenues. Although the acetic acid is not sold, the current acetic acid price is used to approximate the revenue if sold.[27] The remainder of the costs is computed using the same heuristics as the gas-to-methanol plant, and are listed in Table 3.

Subsystem 4.b: acetic acid to ketene to diketene

There are little data available for this process to predict associated costs, as it is new and still in development. However, using the original process patent which shows the bench-scale synthesis processes a guide,[5] a rough sketch of an equivalent continuous is as follows. First, the process begins with the thermal cracking of acetone and then uses a flash drum to handle simple vapor-liquid separation for ketene purification. Then a pressure swing distillation column sequence is used to separate water and acetic acid. A dimerization reactor to convert ketene to diketene, and finally a vacuum-pressure distillation column is used for the final purification step. It should be noted that this is a preliminary design concept that has not undergone a rigorous examination. Instead, the preliminary design is used only to aid in predicting the capital costs of the process. This is achieved by the use of known correlations by Timmerhaus et al.[17] for the costs of the individual process subsystems as a function of their capacity, as shown in Table 6.

In Table 6, ρ_K and ρ_D are the ketene and dikenete densities, respectively; ket_{cap} and dik_{cap} denote the ketene and diketene capacity in tonnes/yr. Using Equations (10) and (11), these variables can be determined from stochiometric ratios.

The operating cost of the plant is estimated in a similar way. Seider et al.[17] describes a method to estimate the number of operators/shift of a process, where every reactor and separator process step (including distillation or evaporation) is considered to be a single section and every section requires 1 operator/shift for fluid processing processes at low to moderate capacities. For the

capacity of 1000 tonne/day of product, the number of operators will be doubled for each section. Then we can estimate that this process requires at least 10 operators/shift for 1000 tonne/day of production. For capacities other than this, Equation (5) is applied. The other operating cost components are estimated in a similar procedure as presented in Table 3.

Table 6. Capital costs of the diketene subsystem. Note that the flash drum has been neglected due to its small size and contribution to the total.

	Plant component	Plant size (1000 m^3/day)	Fixed capital cost (in 2000- million $)	Power factor	Scaled capital cost (million $)
1	Thermal cracking	1.6	6	0.7	$6 \times (\frac{ket_{cap}}{1.6 \times \rho_K \times 330})^{0.7}$
2	Distillation (atm)	16	38	0.9	$38 \times (\frac{ket_{cap}}{16 \times \rho_K \times 330})^{0.9}$
3	Dimerization	1.6	6	0.58	$6 \times (\frac{dik_{cap}}{1.6 \times \rho_D \times 330})^{0.58}$
4	Distillation (vacuum)	16	23	0.7	$23 \times (\frac{dik_{cap}}{16 \times \rho_D \times 330})^{0.7}$
5	Total updated fixed capital cost				$Sum\ of\ 1\ through\ 4 \times (\frac{575}{394.1})$

Subsystem 4.c: diketene to butanol

Like Subsystem 4.b, there is a lack of process data which allows the costs of this process to be computed in detail. Therefore, a simple flowsheet consisting of a hydrogenation reactor and an atmospheric pressure distillation column was synthesized for the purposes of cost estimation. Based on the experimental results of Henri et al.[5] (specifically experiment 5), the conversion of diketene in Equation (12) is over 99%, therefore 100% conversion was assumed for simplicity. The costs were determined using correlations of Timmerhaus et al.[17] using the same procedure described for subsystem 4.b as shown in Table7.

Table 7. Capital costs of the butanol subsystem

	Plant component	Plant size (1000 m^3/day)	Fixed capital cost (in 2000-million $)	Power factor	Scaled capital cost (million $)
1	Hydrogenation	1.6	3.5	0.65	$3.5 \times (\frac{x_1}{1.6 \times \rho_B \times 330})^{0.65}$
2	Distillation (atm)	16	38	0.9	$38 \times (\frac{x_1}{16 \times \rho_B \times 330})^{0.9}$
3	Total updated fixed capital cost				$Sum\ of\ 1\ through\ 2 \times (\frac{575}{394.1})$

In Table 7, ρ_B is the average density of butanol of n-butanol and i-butanol, and x_1 is the capacity of butanol production in tonnes/yr, which is a decision variable of the optimization problem.

The operating costs of the plant are estimated in the same way as subsystem 4.b. This process involves 2 sections and requires 4 operators/shift for 1000 tonne/yr production rate. For other

capacities, Equation (5) has to be applied. The remaining plant costs use the same method as Table 3.

CO_2 Transportation and Purchase (Subsystems 5 and 6)

It is assumed that CO_2 will be brought to the central facility via a pipeline (or pipelines). It is assumed that the delivery price charged for CO_2 (in addition to the sale price) is 15 $/tonne per 1000 km traveled.[31] The distance is determined as the Euclidian distance between the methanol-to-butanol plant location and the location of CO_2 source. The largest 8 emitters of CO_2 in Alberta were selected as potential CO_2 sources, as shown in Table 8. Since it is harder to capture CO_2 when it is more dilute, the costs of capture were estimated based on the CO_2 concentration in the flue gases,[26] which differ from location to location. Although more than eight sources of CO_2 could be considered, each addition would slow down the run time of the optimization algorithm considerably, for marginal changes in the results.

Table 8. CO_2 sources[32]

Facility Name	CO_2(tonnes)	Price[26] ($/tonne)	Latitude (DD)	Longitude (DD)
Mildred Lake and Aurora North Plant Sites	11,745,044	33	57.041	-111.616
Sundance Thermal Electric Power Generating Plant	11,385,738	38	53.808	-113.652
Genesee Thermal Gen. Station	9,333,694	38	53.228	-114.330
Suncor Energy Inc. Oil Sands	8,229,323	35	56.723	-111.362
Keephills Thermal Electric Power Generating Plant	7,904,737	39	53.498	-114.356
Sheerness Generating Station	5,550,107	40	51.634	-111.821
Battle River Generating Station	5,120,895	40	52.541	-112.111
Cold Lake	4,551,848	35	54.824	-111.482

OPTIMIZATION PROBLEM

The purpose of this study is to find the best way of commercializing flare gas/CO_2 –to-butanol process, which in this case considers two competing objectives: profitability and reduced environmental impact. In this study, the profitability is measured by net present (NPV) value, while reduced environmental impact is measured by GHG reduction. To be consistent with other studies that focus on GHG reduction projects in Alberta, GHG reduction is reported in a normalized form called “percentage of emission reduction (PER)”, which is simply equal to the net amount of GHG emissions avoided divided by the total GHG emissions in Alberta (208 Mtonne/yr in 2010):[33]

$$Percentage\ of\ CO_2\ Emission\ Reduction\ (PER) = \frac{(total\ avoided\ CO_2 - total\ CO_2\ emission\ of\ process)}{total\ CO_2\ emission\ in\ Alberta} \quad (16)$$

Table 9. Optimization problem features

Property	
Problem type	Nonlinear problem (NLP)
Objective function	$(1-\lambda)\frac{NPV}{NPV_0} + \lambda\frac{PER}{PER_0}$
Decision variables	Given in Table 1
Constraints	Upper and lower bound of all variables + Equationss (18) and (19)
Solvers	MATLAB-Fmincon, GAMS-BARON
NPV_0 (million $)	305.988
PER_0 (%)	0.20

In other words, a PER of 1% would imply that by using the process, the total net GHG emissions in Alberta would be reduced by 1%. In this case (as will be shown in section 4), maximizing NPV and maximizing PER are directly competing objectives. Therefore, the two objectives are combined into one weighted objective function as follows:

$$Objective\ function = NPV\_PER = (1-\lambda)\frac{NPV}{NPV_0} + \lambda\frac{PER}{PER_0} \quad (17)$$

Where normalization factors NPV_0 and PER_0 are respectively the maximum NPV and PER (given in Table 9) and were obtained by solving the optimization problem by maximizing each objective function separately. λ is the weight factor between 0 and 1 that balances the importance of each objective function. A full range of λ was examined to determine how changing the relative importance of profit to environmental benefit affects the optimization results.

In addition to the model equations, the constraints of optimization problem are the upper and lower bounds for all of the 194 decision variables and two following mass balance equations:

$$x_1 = 0.3285\sum_{j=1}^{76} n_f(j) + 1.4787\sum_{i=1}^{100} n_g(i) + 0.9253\sum_{k=1}^{4} n_m(k) \quad (18)$$

$$x_1 = 0.6737\sum_{n=1}^{8} n_c(n) \quad (19)$$

The above correlations are derived from mass balances based on Equations (2), (6) and (7). The other features of optimization problem are shown in Table 10. Note that the upper bound on the butanol production capacity was set at 138 million L/yr, which is based on certain criteria specific to Pioneer Energy.

Note that there are no integer variables in this formulation, although the model still retains its discrete characteristics. For example, in reality, MAGS/PERT-2 units are purchased only in integer quantities. As such, a smooth, continuous approximation of the "ceiling" function is used to compute the number of MAGS/PERT-2 units required at each flare gas location. Consider the following function:

$$g(y) = \frac{1}{2}\left(\frac{e^{\alpha y} - e^{-\alpha y}}{e^{\alpha y} + e^{-\alpha y}} + 1\right) \quad (20)$$

where y is a variable and α is a tuning parameter. $g(y)$ is a smooth function such that $g(0) = 0.5$, $\lim_{y\to\infty} g(y) = 1$ and $\lim_{y\to-\infty} g(y) = 0$. However, for sufficiently large α, $g(y)$ is very close to 1 for small positive y and $g(y)$ is very close to 0 for small negative y. Thus, $g(y)$ is a smooth approximation of a step function. Next, consider the ratio of flare gas used at location i to the capacity of one MAGS/PERT-2 system:

$$x_i = \frac{n_{fi}}{4702.5(\frac{tonne}{yr})} \quad (21)$$

Based on the largest flare gas source considered in this study, x_i can vary between 0 and 8. Therefore Equation (20) can be used to estimate the number of required MAGS/PERT-2 systems required to process n_{fi} tonne/yr of flare gas as follows:

$$ceil\,(x_i) \approx g(x_i) + g(x_i - 1) + g(x_i - 2) + g(x_i - 3) + g(x_i - 4) + g(x_i - 5) + g(x_i - 6) + g(x_i - 7) + g(x_i - 8)\ ,\ 0 \le x_i \le 8 \quad (22)$$

This equation gives an acceptable approximation of $ceil(x_i)$ in most cases where flare gas is used, especially when α is large enough. However, the approximation is not good when the amount of flare gas used just happens to be very close to an exact integer multiple of the capacity of a PERT-2 unit. This is very unlikely for cases when flare gas is used ($n_{fi} > 0$), but this error occurs every time that flare gas is not used ($n_{fi} = 0$). To solve this problem, the approximation of $ceil$ is modified such that $g(y)$ is shifted to the right by a small ϵ as follows:

$$ceil\,(x_i) \approx g(x_i - \epsilon) + g(x_i - 1 - \epsilon) + g(x_i - 2 - \epsilon) + g(x_i - 3 - \epsilon) + g(x_i - 4 - \epsilon) + g(x_i - 5 - \epsilon) + g(x_i - 6 - \epsilon) + g(x_i - 7 - \epsilon) + g(x_i - 8 - \epsilon)\ ,\ 0 \le x_i \le 8\ ,\ \epsilon > 0 \quad (23)$$

This ensures that when x_i is zero, Equation (23) returns a number very close to zero, but all other approximations are virtually unchanged. As a result, the values computed by Equation (23) are very close to the correct integer value for all flare gas usage values used in this study (all were within 1% when using $\epsilon = 0.15$ and $\alpha = 22$). This means that the capital cost predictions for the MAGS/PERT-2 units used in the model have only 1% error at most.

Although a true ceiling function could have been used to ensure that the number of MAGS/PERT-2 units is exactly an integer value, this creates non-smoothness in the model which makes it unusable in solvers such as BARON. Alternatively, the model could have been reformulated using integer variables, but preliminary studies showed that an MINLP formulation resulted in excessively long computation times (could not solve after several days). Therefore, the continuous NLP formulation was preferred since global optima could be found quickly with BARON with only a negligible introduction of model error. Also, it should be noted that after the NLP optimization was completed in BARON, the objective function was re-calculated using the same decision variables, except slightly modified to use the true integer values for the number of PERT-2 units purchased (for example, instead of computing the capital costs of 2.001 PERT-2 units, exactly 2 units were considered instead). In almost all cases, the objective function changed negligibly, with a 3% deviation in the worst case. All results in this paper are presented using the updated objective functions with the true integer values for the number of PERT-2 units.

In addition to using BARON in GAMS, the use of fmincon in MATLAB to solve the NLP was also investigated. Although fmincon cannot determine global optimality by computing the optimality gap, it is useful for finding different local optima by resolving the NLP using different initial guesses. In addition, fmincon was used to solve a variant of the NLP which used rounding functions instead of the smoothing function shown in Equation (23) in order to verify that the approximate error introduced by using the smoothing function was negligible.

Net Present Value Parameters

The NPV is a metric which examines profits along with other important factors which affect the business including debt and equity payments, cash flow, inflation, taxes, and depreciation. The method of Seider is used to compute the NPV.[20] Key assumptions required for this analysis can be found in Table 10. The debt-to-equity ratio, equity return rate, and interest rate are values

recommended by the US Department of Energy for new kinds of liquid fuels plants.[34] Furthermore, to estimate plant depreciation, MACRS depreciation tax table was used.

Table 10. Parameters of NPV calculation

Parameters	Values	Comment
Interest rate on loan	10%	Common for new kinds of chemical plants
Inflation	2.79%	
Debt percentage	50%	Suggested by US DOE for new kinds of liquid fuel plants
Tax rate (federal + province)	34%	Sum
Equity return rate	20%	Suggested by US DOE for new kinds of liquid fuel plants
Loan life time	30 yr	Commonly used in analyses of this type
Plant life time	30 yr	Commonly used in analyses of this type

PER Calculation

In order to compute percentage of CO_2 emission reduction (PER), data were collected or estimated on each process step. Then, the total CO_2 emitted or avoided for each case could be computed considering the sum of the contributions at each process step. CO_2 emissions considered in this work includes direct CO_2 emitted to the atmosphere in the exhaust gas of each process, as well as indirect CO_2 emissions associated with the transport of materials due to transportation fuel combustion. In addition, indirect CO_2 emissions from creation of purchased methanol, natural gas, and hydrogen are also accounted. Avoided CO_2 includes any purchased CO_2 consumed by the methanol-to-butanol process, which assumes that any CO_2 captured would have been otherwise emitted to the atmosphere, and neglects the indirect emissions associated with CO_2 capture. In addition, avoided CO_2 includes any CO_2 that would have been emitted from

Table 11. CO_2 Avoided/Emitted by each process step

Subsystem	Subsystem Figure 1	CO_2 emission
Natural Gas Purchase	1.a	0.14 tonne CO_2 emitted per tonne of pipeline gas bought[35]
MAGS/PERT-2	1.b, 2.c	1.7193 tonne CO_2 avoided per tonne of flare gas used
Methanol Purchase	2.a	0.5429 tonne CO_2 emitted per tonne of methanol bought[36]
Bio-Methanol Purchase	2.a	0 tonne CO_2 emitted per tonne of methanol bought (assumed)
Gas-To-Methanol Plant	2.b	0.4553 tonne CO_2 emitted per tonne of methanol produced[36]
Methanol Train Transport	3	0.01739 tonne CO_2 emitted per tonne MeOH per 1000 km[37]
Acetic Acid Production	4.a	0.2 tonne CO_2 emitted per tonne acetic acid produced[36]
Diketene Production	4.b	0 tonne CO_2 emitted per tonne of diketene produced (no data)
Butanol Production	4.c	0 tonne CO_2 emitted per tonne of butanol produced (no data)
Hydrogen Purchase	4.d	8.5 tonne CO_2 per tonne hydrogen purchased[38]
CO_2 Pipeline Transport	5	9.50×10^{-5} tonne CO_2 emitted per tonne CO_2 per 160 km[39]
CO_2 Purchase	6	1 tonne CO_2avoided per tonne CO_2 purchased (assumed)

flare gas combustion but was avoided due to the use of a MAGS/PERT-2 device. Some process subsystems have no data available on CO_2 emissions, and so these are neglected. Construction, commissioning, and decommissioning are also not considered. Biomethanol is also assumed to have zero CO_2 emissions associated with production since it derives from bio wastes, although in reality some CO_2 emissions are to be expected. However, the neglected emissions are expected to constitute only a small percentage of the total lifecycle CO_2 emissions and so the resulting life cycle analysis is suitable for our analysis. A more rigorous analysis including these details and other environmental impact factors is a subject of ongoing research. The CO_2 emissions per tonne of product/feed for each subsystem are summarized next. Where known, GHG emissions include other GHGs, such as CH_4 and NOx, and are converted to CO_2 equivalents ("CO_2e").

The CO_2 emitted from flare gas burning can be calculated from the flare gas composition. Johnson and Coderre reported the mean flare gas composition,[40] which is summarized in table 12. By assuming that the flare gas is completely combusted (all alkanes react with oxygen to CO_2, not CO or other hydrocarbons), reaction stoichiometry can be used to predict a conservative estimate of 2.579 tonne CO_2 emitted per tonne of flare gas burned can be computed. However, since the MAGS/PERT-2 co-produce other products which are not included in this supply chain, only some of the CO_2 avoided per tonne of flare gas used can be attributed to the methanol produced. For MAGS/PERT-2, only about 67% of the flare gas goes to methanol production, resulting in a final allocated value of 1.7193 tonne CO_2 avoided per tonne flare gas consumed.

Table 12. Average flare gas composition[40]

Component	Mole fraction	Mass fraction	Tonne CO_2/Tonne Flare Gas
C_1	0.85	0.6967	1.9116
C_2	0.05	0.0768	0.2248
C_3	0.025	0.0563	0.1686
i-C_4	0.005	0.0148	0.0448
n-C_4	0.01	0.0297	0.0900
C_5	0.006	0.0221	0.0674
C_6	0.003	0.0132	0.0404
C_7^+	0.002	0.0102	0.0314
N_2	0.03	0.0429	
CO_2	0.0125	0.0281	
H_2S	0.005	0.0087	
H_2& He	~0.0015	$\sim 3\times10^4$	
Total CO_2			2.579 tonne CO_2 per tonne flare gas

RESULTS

This section will discuss the results of optimization by single and multi-objective functions. To summarize, the results of maximizing NPV show that the most profitable supply chain also has the most GHG emissions. Conversely, when PER objective function was maximized, the resulting supply chain had in a net negative amount of GHG emissions, but the profitability was not satisfactory. However the results of maximizing multi-objective function are very promising and provide several supply chain networks which are both profitable and have a net negative GHG emission.

Results for λ=0 (Maximizing NPV)

This case is the same as maximizing the NPV objective function. The problem is solved using BARON solver; the total elapsed time was only few seconds and optimality gap was 0.0001, meaning that the solution is the global optimum solution, within tolerances. Table 13 summarizes the results of this case. As the results show, the process is highly economic (a NPV over $300 million), however, the PER is negative which means that net GHG emissions are positive. Also the results indicate that for this case, it is better to construct a gas-to-methanol plant and purchase pipeline natural gas, rather than capture flare gas via the portable technology. It should be noted that although the Fmincon solver usually can yield the same results as BARON for each case (λ=0) for the right initial guesses, the optimization time is considerably higher for Fmincon solver than BARON.

Furthermore, the optimization algorithm always chooses to locate the gas-to-methanol and methanol-to-butanol plants at the same location, which is at the same location as the natural gas pipeline connection point. In this case, the optimal location is in eastern Alberta (at -111.280DD, 56.648DD).This choice eliminates the need for a natural gas pipeline and methanol transportation cost from methanol plant to central facility. The optimal CO_2 source is Mildred Lake and Aurora North Plant Sites (-111.616DD, 57.041DD). This choice effectively reduces the cost of CO_2 pipeline and avoids constructing gas pipelines or shipping methanol. This is true at any capacity considered and is depicted graphically in Figure 3. In this case, the optimal CO_2 source is not actually the nearest geographically to the chosen plant location because the nearer CO_2 source has a higher cost of CO_2 due to a more dilute flue gas. The optimizer has determined that it is better to build a longer pipeline to the cheaper source.

Table 13. Optimization result for maximizing NPV (λ=0) and PER (λ=1) with BARON solver

Property	NPV maximizing results (λ=0)	PER maximizing results (λ=1)
Optimality gap	0.0001	0.0001
CPU time	12 seconds	12 seconds
PER (%)	-0.063	0.20
NPV (million $)	305.988	-85.8
Optimal Natural gas pipeline connection	-111.280DD, 56.648DD	Not selected
Optimal Gas-To-Methanol plant location(p_{2x}, p_{2y})	-111.280DD, 56.648DD	No MeOH plant
Optimal Methanol-To-Butanol plant location (p_x, p_y)	-111.280DD, 56.648DD	-114.878 DD, 53.457 DD
Optimal CO_2 Source	Mildred Lake and Aurora North Plant Sites (-111.616DD, 57.041DD).	Mildred Lake and Aurora North Plant Sites (-111.616 DD, 57.041 DD)
Fixed capital investment (million $)	130.8	406.1
Operating costs (million $)	161.08	202.9
Revenue (million $)	246.97	249.6
BuOH capacity, x_1 (tonne/yr)	111,780	111,780
Total MeOH used (tonne/yr)	120,800	120,800
MeOH purchased (tonne/yr)	0.0	8547.360
Flare gas consumed (tonne/yr)	0.0	316,166.2
Natural gas purchased (tonne/yr)	75,593	0.0
Number of PERT-2 trucks	0	104
Total consumed CO_2 (tonne/yr)	165,920	165,920

In order to find profitability variation with plant capacity (x_1), the problem was run with the added constraint that the butanol capacity (x_1) is fixed at a certain amount. Figure 4 shows the results of this analysis which indicates that NPV increases almost linearly as plant capacity increases, therefore operating at the maximum possible capacity leads to maximum profit. Also, the minimum profitable capacity (that which has NPV=0), is at approximately 25,390 tonne per year of butanol produced. However, for any of the capacities considered, the global optimum result was always that all of the methanol used for the methanol-to-butanol process should be made by purchasing natural gas from a conventional gas pipeline and then constructing a gas-to-methanol plant. No flare gas sources or commercial methanol sources were selected in any of these cases since it was simply more profitable to use the gas-to-methanol route. There is

sufficient pipeline gas available at a single pipeline connection, even at the maximum production capacity considered. In Figure 4.b, the fixed capital investment increases nonlinearly with pant capacity due to economies of scale. As shown in Figure 4.c, the PER value is negative for all considered capacities, which demonstrates that considering only the economic objective is not enough to achieve both profitability and environmental benefit.

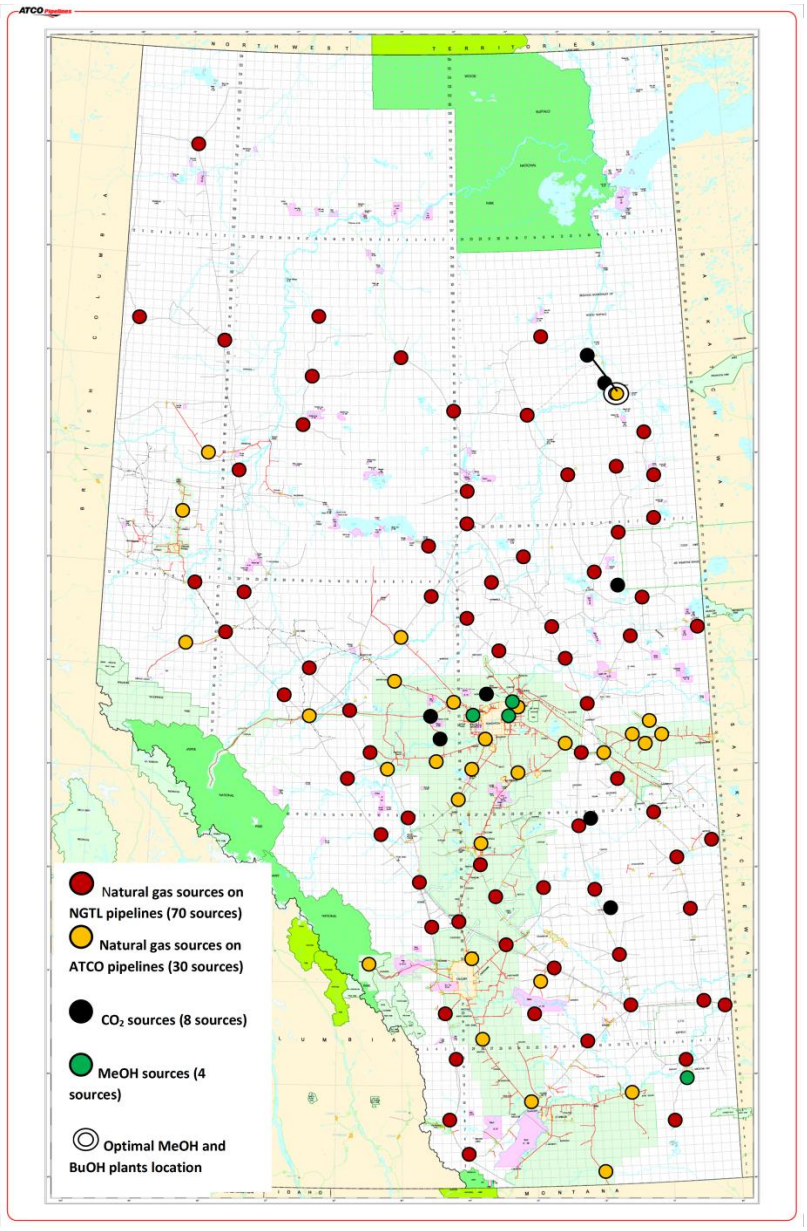

Figure 3. Optimal network for maximizing Equation (17) with λ=0. Black lines show the connections from the chosen plant location to the chosen CO_2 sources. The global optimal methanol and butanol plants location is the white ring surrounding the chosen natural gas source.

By using different initial guesses, the Fmincon solver finds many other local optimum solutions which have only slightly lower NPV, though with different locations of the pipeline connection point, centralized gas-to-methanol, and methanol-to-butanol plants (which are always together at the same location) and the CO_2 source. The slight differences arise from the different prices of CO_2 at each source and distances from the nearest natural gas pipeline connection. All of these solutions suggest only one CO_2 source and one natural gas source in the closest vicinity of that CO_2 source. This means that every CO_2 source with a close natural gas source is potentially a reasonable solution. None of the flare or methanol sources are selected in any of the other candidate cases. If other factors like land price, access to transportation facilities, labour, and other conditions are taken into account, then any of these other possible local optimal solutions might be the best option for a business. Table 14 lists some of these local solutions.

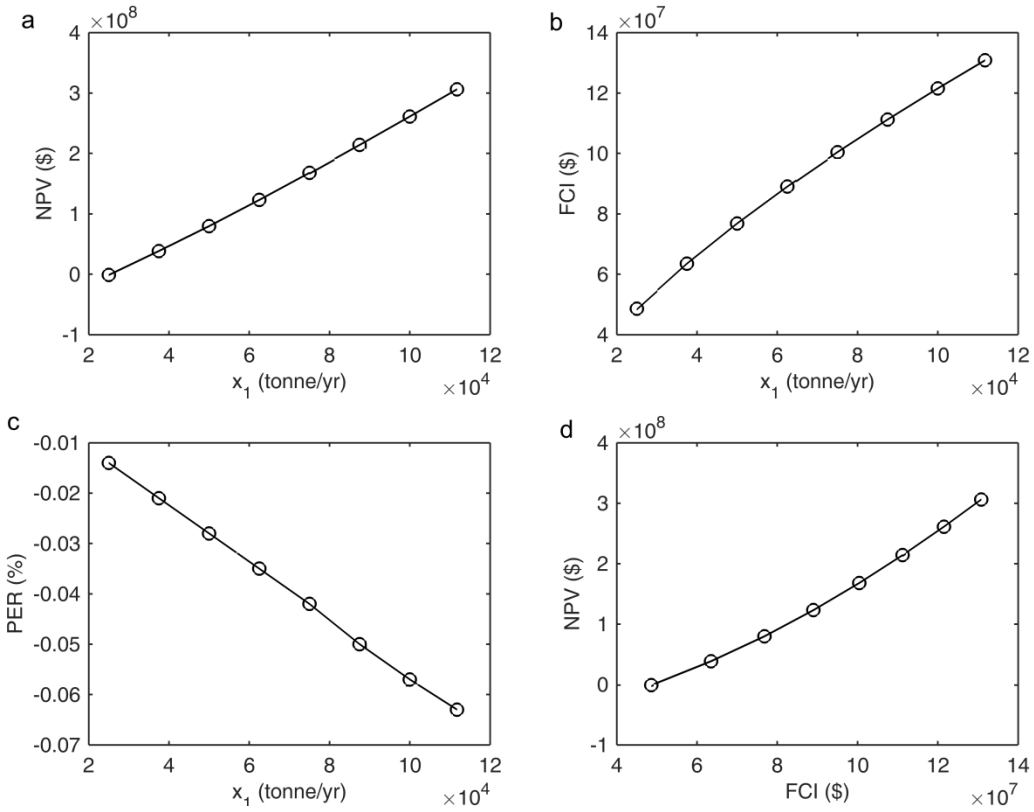

Figure 4. (a)NPV vs plant capacity (b) Fixed capital investment (FCI) vs plant capacity (c) PER vs plant capacity. (d) NPV vs FCI

Results for λ=1

This case considers only maximizing the PER objective function and does not take profitability into account when choosing the best configuration to use. In other words, this objective tries to

find the most environmentally friendly solution, without considering profit. The problem was re-run with these new considerations for the largest butanol production rate case. It should be noted that this case has more than one global solution, depending on optimization initial guesses. The reason for multiple solutions is that there are many possible optimal configurations which give the same PER and different NPVs. However, the difference is only in the optimal location of the plants and CO_2 sources which causes different NPV values. The third column of Table 13 shows one of the best possible answers. The optimal strategy for this answer uses 104 PERT-2 trucks, effectively using all of the available flare gas and bio-methanol, and no purchased natural gas. Because the use of flare gas and bio-methanol avoids a considerable amount of CO_2 emissions, the PER is a much more favourable 0.20%, meaning that by capturing the flare gas and constructing the methanol-to-butanol facility, the total emissions in Alberta would actually be reduced by 0.20% per plant constructed. However, the NPV in this case is $-85.8 million and fixed capital cost increases to $406.1 million. Although this is not an economical realistic solution, it provides an upper bound on CO_2 emission reduction.

Table 14. Some of the local optimums, as predicted by Fmincon solver.

Optimal CO_2 Source	Optimal p_x, p_y, p_{2x}, p_{2y} and natural gas sources	NPV ($\$10^6$)	FCI ($\$10^6$)	Operating costs ($\$10^6$)	Revenue ($\$10^6$)	x_1 (tonne /yr)	MeOH used (tonne /yr)
Mildred Lake and Aurora North Plant Sites	(-112.482, 57.259)	305.38	131.1	161.21	246.98	111,780	120,800
Sundance Thermal Electric Power Generating Plant	(-114.148, 53.714)	301.76	130.9	162.05	246.98	111,780	120,800
Genesee Thermal Generating Station	(-114.148, 53.714)	301.76	130.8	162.06	246.98	111,780	120,800
Suncor Energy Inc. Oil Sands	(-111.280, 56.648)	304.58	130.8	161.43	246.97	111,780	120,800
Keephills Thermal Electric Power Generating Plant	(-114.148, 53.714)	300.95	131.0	162.21	246.98	111,780	120,800
Sheerness Generating Station	(-112.020, 51.864)	300.84	130.8	162.25	246.97	111,780	120,800

Pareto Optima

In this set, the objective function was modified as Equation (17) to consider both economic and environmental factors. All global optimum solutions that could be found occurring between $0 \leq \lambda \leq 1$ are presented in Table 15. The results show that for some values of λ there are two non-unique global optimal solutions with the same objective function value within tolerances. Also the results clearly reflect the discontinuous and discrete nature of the model, since each global optimum solution was found within a certain range of λ, but the global optimal solutions in adjacent regions of λ are different from each other in discrete ways (such as having more or less PERT-2 units, or using or not using certain flare gas sites). For example, the global optimal solution at $\lambda = 0.5375$ uses 12 fewer flare gas sources than the solution at $\lambda = 0.5375 + \delta$ for some small δ. It should be noted that, flare gas sources are selected, they are often not used at the maximum capacity. Because the number of MAGS/PERT-2 units purchased is discrete, in many of cases it is not optimal to capture the entire flare gas source if one of the units operates much below capacity.

Figure 5 depicts the Pareto curve graphically using the results of Table 15. Non-unique solutions for λ=0.425 and 0.6069280 are indicated with two pink and red points, respectively. It is apparent in the curve that the non-unique solutions form the bounds of large gaps in the Pareto curve. Those large gaps correspond to significant differences in the character of the optimal solutions. For example, in the λ=0.425 case, one of the non-unique solutions uses flare gas while the other uses no flare gas. In the λ= 0.6069280, one of the non-unique solutions uses conventional natural gas and the other does not. Small maps illustrating the full results are shown beside a few selected points on the Pareto curve. Figure 5 demonstrates that in the range of λ=0.425 to 0.59, it is possible to construct a process and supply chain such that the net GHG emissions in Alberta are actually reduced (PER>0) will still yielding satisfactory profitability (NPV>0). Also, when flare gas is used, the optimal methanol-to-butanol plant location is always somewhere within the vicinity of Edmonton and the area to its West. As more flare gas sites are added, the largest ones are chosen first regardless of its location. If more flare gas sites are used, the sites in the southeastern portion of Alberta are added next, followed by sites in the northwest last.

Table 15. All known global optimal solutions as a result of maximizing Equation (17), for various values of λ with the BARON solver. The optimality gap for all cases was 0.0001 and only a few seconds were required for each run.

λ	NPV (million $)	PER (%)	Objective Function Value	Uniqueness of Solution	# CO_2 sources	# convent. gas connections	# flare gas sources used	# methanol suppliers used
0	305.8135	-0.063	1	unique	1	1	0	0
0-0.425	305.8135	-0.063	>0.4411	unique	1	1	0	0
0.425	1) 305.8135 2) 218.5790	1) -0.063 2) 0.014	0.4411	non unique	1 1	1 1	0 9	0 0
0.43	205.9361	0.025	0.43758	unique	1	1	10	0
0.4305	179.4576	0.048	0.43736	unique	1	1	12	0
0.4315	175.2792	0.052	0.43708	unique	1	1	14	0
0.432	158.2740	0.066	0.43705	unique	1	1	16	0
0.433	154.4388	0.07	0.4369	unique	1	1	17	0
0.44	145.2828	0.077	0.43635	unique	1	1	19	0
0.45	141.4792	0.08	0.43555	unique	1	1	19	0
0.46-0.48	133.7475	0.087	0.43522	unique	1	1	20	0
0.49	113.3440	0.101	0.4360	unique	1	1	24	0
0.50	110.1144	0.103	0.4376	unique	1	1	24	0
0.52	104.0436	0.106	0.4407	unique	1	1	25	0
0.53-0.5375	100.2189	0.109	0.4425	unique	1	1	26	0
0.538	65.42937	0.128	0.4446	unique	1	1	38	0
0.54	619.3345	0.13	0.4452	unique	1	1	39	0
0.55	54.61178	0.134	0.44971	unique	1	1	40	0
0.555-0.59	12.93452	0.157	0.45696	unique	1	1	52	0
0.595-0.6	-13.9377	0.169	0.48552	unique	1	1	59	0
0.6069280	1) -13.9750 2) -76.1215	1) 0.169 2) 0.196	0.49617	non unique	1 1	1 0	65 76	0 1
0.6069280-0.65	-76.1551	0.196	0.54905	unique	1	0	76	1
0.65-1	-88.05	0.200	<0.6112	unique	1	0	76	1
1	-88.05	0.200	1	non unique	1	0	76	1

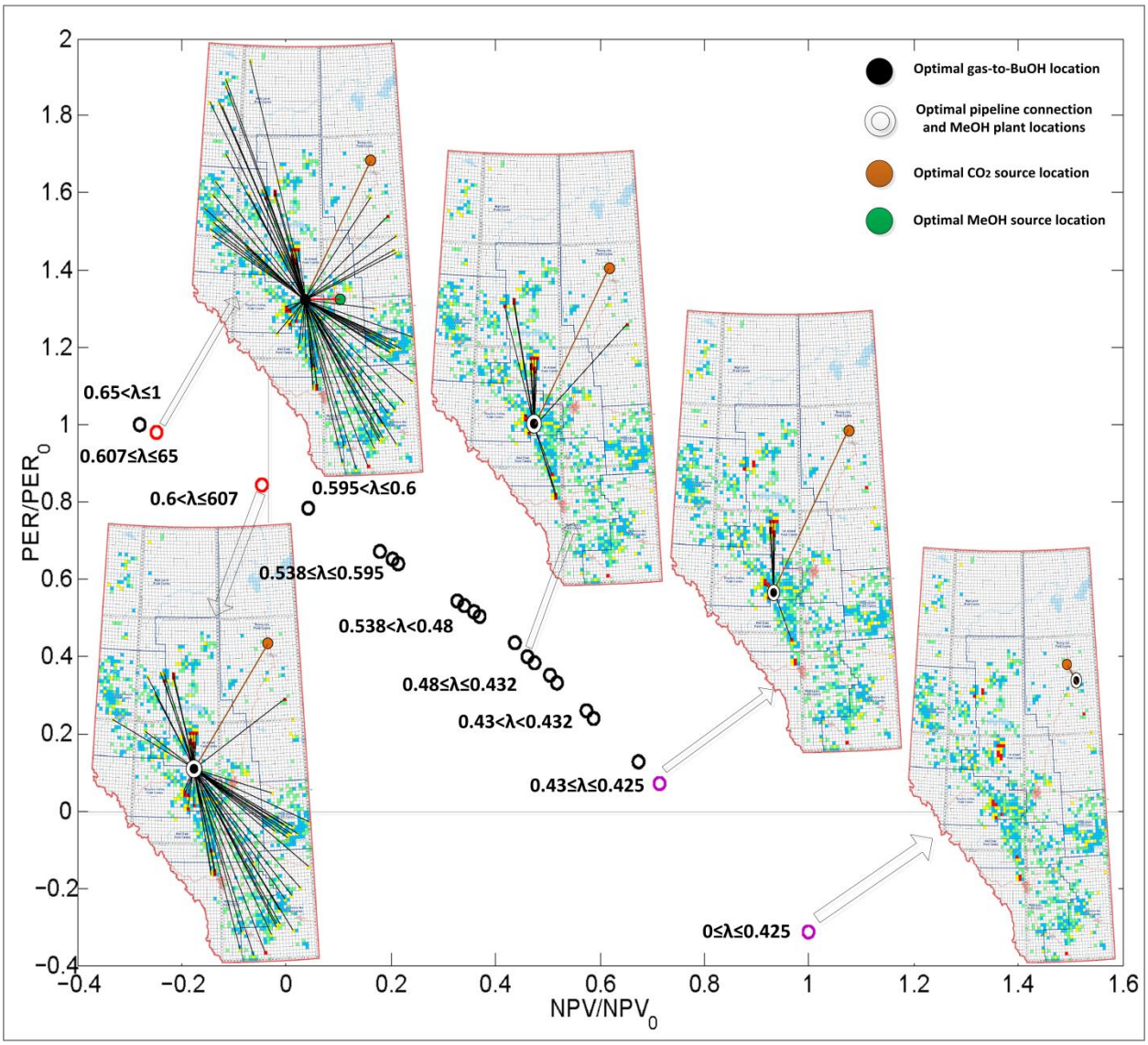

Figure 5. Pareto curve, pictures around the points show the best network for that specific solution, also nonunique answers at the same λ are distinguished from other points with magenta (λ=0.425) and red colors (λ=0.6069280)

Although Fmincon was effective at arriving at the global optimal solutions or other solutions very close to it for the maximizing NPV case (λ=0), it was not able to find good solutions for other λ, and it took an unreasonably long amount of time (sometimes over 40 minutes, compared to just 4 seconds with BARON).

Sensitivity Analysis

Because of the uncertainty of the parameters, a sensitivity analysis was performed. Starting with the solutions from the maximum NPV objective function results, selected parameters were perturbed by plus or minus 25% from their solution value individually, and the NPV was

recalculated by rerunning the optimization problem with BARON to global optimality with a gap of 0.0001. The results for the maximum production case are shown in Table 16.

The results indicate that most sensitive parameters are the BuOH selling price and the tax rate. However, the results show that, if the selling price of butanol decreased by 31.08 % to $4.2269 /gal, the NPV will be zero. In other words, this is the minimum butanol selling price required to make a profit.

Table 16. Sensitivity analysis for ±25% change from the base case (111,870 tonne/yr case)

Parameters	Base case	ΔNPV% for -25% changes in parameters	ΔNPV% for +25% changes in parameters
CO_2 price	$33-40/tonne	2.04	-2.04
Natural gas	$184.21/tonne	5.19	-5.19
Fixed capital Investment	$130.83 million	7.01	-7.01
BuOH selling price	$2,000/tonne	-79.15	79.15
Tax rate	34%	13.23	-13.23
Operating costs of gas-to-methanol plant	$31.81 million/yr	11.85	-11.85
Operating costs of Acetic acid subsystem	$30.63 million/yr	11.42	-11.42
Plant life time	30 year	-3.92	1.37

CONCLUSIONS

In this study, an optimization problem has been developed to predict the best strategy of commercializing a novel, sustainable butanol production process while ensuring that the net GHG emissions in Alberta are reduced. A model was constructed which considers a supply chain superstructure considering different sources or pathways for various materials flowing through the supply chain and different potential technologies. The model was structured with low-error smoothing functions such that the optimization framework could be formulated as an NLP while still retaining the discrete and discontinuous nature of the problem. This made it possible to find global optimal solutions using BARON in only a few seconds. By testing economic and environmental objective functions separately, it was found that considering only one objective cannot guarantee obtaining both environmental and economic goals. A weighted objective function approach was used to consider the competing objectives in a Pareto analysis.

It was found that it is possible to construct a process which uses a combination of novel mobile flare-gas-to-methanol systems at up to 52 different flare gas locations, a traditional gas-to-methanol process, and a novel methanol-to-butanol process that not only is profitable for the

company but results in a net *decrease* in GHG emissions in Alberta by up to 0.157% thanks to cessation of gas flaring. This is the emission reduction that can be achieved through one plant and this does not include any additional benefits from avoided CO_2 that might be obtained by displacing petroleum-based gasoline with the butanol produced. In addition, it is more profitable to avoid the use of flare gas altogether and instead build a traditional gas-to-methanol process, but does not have an environmental benefit since it still produces net GHG emissions and the status quo of wasteful gas flaring continues. Therefore, to incentivize flare gas capture, government benefits such as carbon tax credits may be necessary. A study of the kind and amount of government benefit necessary to incentivize flare gas capture is a subject of future research.

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NOMENCLATURE

Abbreviations

dik	diketene
FCI	fixed capital cost
GHG	greenhouse gas
ket	ketene
LHV	Lower heating value
MAGS	mobile alkane gas separator
MINLP	mixed integer nonlinear programming
NLP	nonlinear programming
NPV	net present value
OPL	operating labour cost
PER	percentage of emission reduction
PERT-2	portable enhanced oil recovery Technology-2

Subscribes

B	butanol
c	carbon dioxide
cap	capacity
D	diketene
f	flare gas
g	natural gas
K	ketene

x	longitude
y	latitude

Greek Letters

α	tuning parameter
ϵ	epsilon
λ	weight factor
ρ	density

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