CARBON CAPTURE, UTILIZATION & STORAGE CONFERENCE

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Anthropogenic CO_2 as a Feed/Ingredient in Industrial/Agricultural Processes

Conversion of Captured CO_2 to C4+ Synthetic Chemicals and Drop-In Liquid Fuels

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Acknowledgements & Disclaimer

This is preliminary analysis that has not gone through peer-review yet.

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Abstract

The new process works by combining CO_2 with additional carbon from a variety of low-value natural gas sources, including flare gas, landfill biogas, raw natural gas, etc., to produce high-value C4+ chemicals and liquid fuels through a unique thermochemical route via ketene/diketene intermediaries. This technology has been successfully scaled to 10 L/day on funding from the Canadian government (CCEMC). The process would allow significant amounts of CO_2 emissions to be converted to liquid fuels, polymers, and industrial chemicals. The process involves using feedstocks of CO_2 in combination with other waste carbonaceous feedstocks to form C4+ chemicals, including butanol, heptanol, heptane, isooctane, and higher, which can be used as industrial chemicals and fuels. The economic synthesis of C4+ chemicals is desirable because of their current use as commodity chemicals and solvents in industry, and proven suitability as drop-in automotive fuels. The higher caloric value of butanol and heptanol, 36 MJ/kg and 39 MJ/kg, respectively, is significantly higher than ethanol's 30 MJ/kg. The process starts with a dry reforming reaction to convert CO_2 to form syngas, which is a step of the process which has been demonstrated for NASA at high yield in prior research. Syngas is then converted to methanol, the methanol is then converted to acetic acid, and the acetic acid is then converted to ketene, which are all known industrial processes. Next, our new process is used in the conversion of diketene to butanols and C4+ chemicals via our innovative ketene/diketene hydrogenation chemistry. This part of the process includes synthesis of diketene from ketene, immediately followed by its reduction to butanol and other C4+ chemicals. Heptanol and heptane can be produced from diketene via an additional step via dehydroacetic acid (DHAA) intermediary. We have performed all these integrated reactions in a continuous flow process at 10 L/day under Canadian government (CCEMC) funding, achieving high yield and selectivity (>82%). The process is unique in that it can accept a variety of wasted or low-cost carbonaceous feedstocks in addition to CO_2. Natural gas, flare gas, and biomass were successfully reformed into syngas which can be fed into this process as part of a prior RPSEA project. Over 6 patents have been granted in the US, and many more are pending internationally. We are partnering with a major chemical company in Canada to scale the process, demonstrate commercial feasibility, and ultimately implement it in their production facilities. This process would also allow other low-value or wasted carbonaceous sources, such as agricultural/forestry residues, cellulosic biomass, energy crops, and so on, to be utilized for synthetic chemical and liquid fuel production avoiding many of the problems of existing thermochemical processes, such as Fischer-Tropsch and Methanol-to-Gasoline (MTG).

Wasted flare gas is both an economic & environmental problem

North Dakota from Space

Alberta from Space

***In 2014…** only 10.8% reduction in ND from oil price drop in 2016*

Alberta, Canada flared 1.1 **billion** cubic **meters** per year ……. 39 BCF/yr

North Dakota flared 120 **billion ft^3** per year ……………………..120 BCF/yr *[107 BCF/yr in 2016]*

World flared 7 **trillion** ft^3 (TCF) per year …………………….... 7,000 BCF/yr

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Potential Utilization in Alberta

Flaring in Alberta today

2.1 % of Alberta's GHGs originate from flaring & venting

868 million m³ gas flared/year

333 million m³ gas vented/year

6-8 million tons CO_2-e/year

Could be used to produce

1.4 million tons fuel

Worth $1.2 billion

Basic Chemistry of the Process

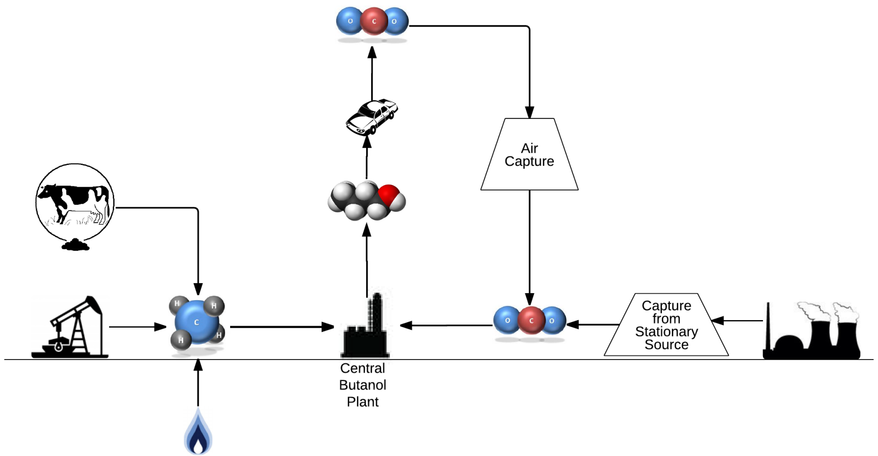
Captured CO_2 From Stationary Source Or Air Capture

Butanol

$$3CH_4 + CO_2 \rightarrow C_4H_9OH + H_2O$$

Water

Flare gas
Landfill gas
Natural gas
Etc.

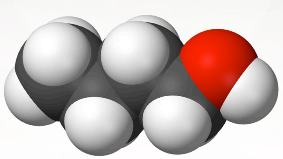


For every 3 CH_4 from flare gas, we consume 1 CO_2 from flue gas, and produce 1 butanol & 1 water.

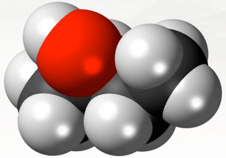
We put carbon that would otherwise be released as CO_2 from flare gas & flue gas back into fuel, polymers, and chemicals!

What is Butanol?

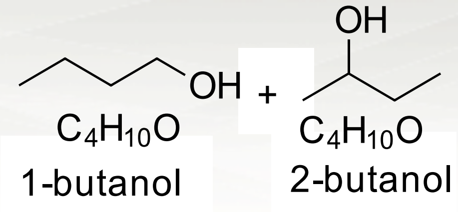
- Butanol is a 4-carbon alcohol *(versus methanol – 1C, ethanol – 2C)*
- Chemical formula C_4H_9OH



1-butanol



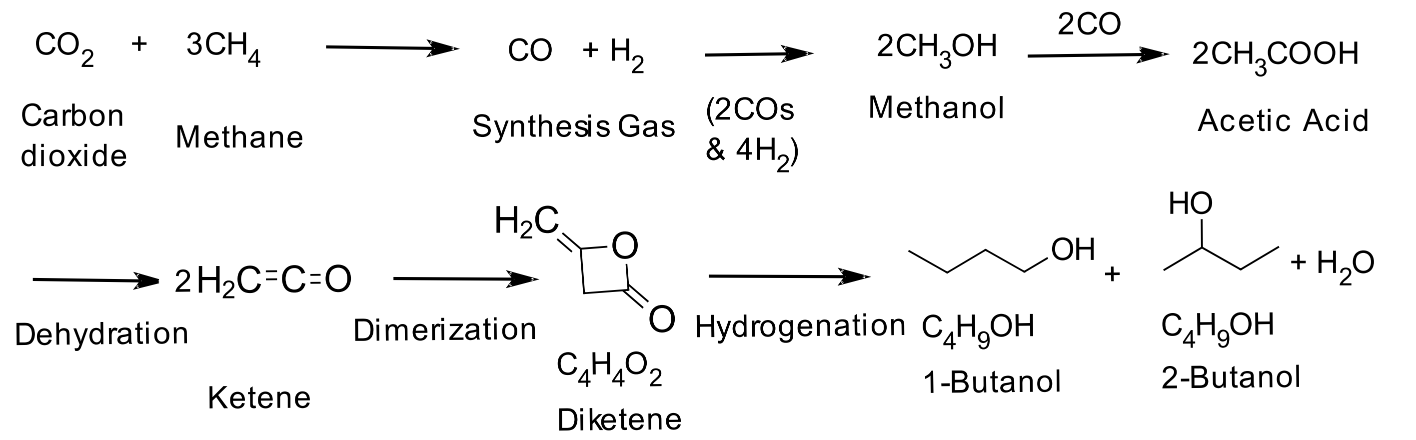
2-butanol



Energy Density: ~36 MJ/kg

- Has 80% the energy content of gasoline
- Fully compatible with existing gasoline engines & pipeline infrastructure. It is a drop-in fuel approved by the EPA for use up to 15% in cars.
- It is an important industrial chemical with an estimated market of over $5 billion per year, used in polymers like acrylates, solvents for paints and pharmaceuticals, and currently made from petrochemical sources.

Detailed Chemistry of the Process



We have developed a novel process to synthesize butanol using scalable acetyl chemistry:

1. Syngas (CO/H_2) production from CH_4 — Known *(e.g., Enerkem trash-to-methanol)*
2. Reverse water gas shift of CO_2 to CO/H_2O — Demonstrated by Pioneer for NASA *at >98% carbon efficiency*
3. Methanol production from syngas — Known *(e.g., Enerkem trash-to-methanol)*
4. Acetic acid production from methanol — Known *at full plant scale*
5. Ketene production from acetic acid — Demonstrated by Pioneer for CCEMC *at 10 L/day scale*
6. Dimerization of ketene to diketene — Demonstrated by Pioneer for CCEMC *at 10 L/day scale*
7. Reduction of diketene to butanols via MAA — Demonstrated by Pioneer for CCEMC *at 10 L/day scale*

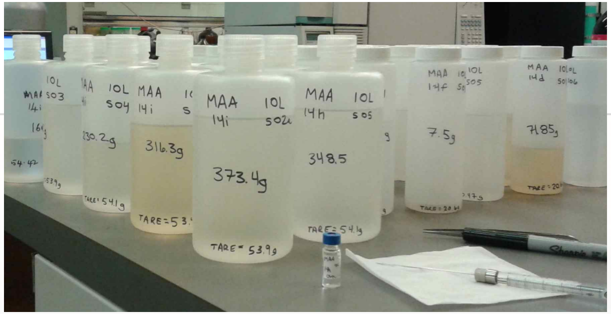
Process at 10 L/day Scale Demonstrated

- The first half of this process, taking **methane to synthesis gas to methanol and then to acetic acid**, is already proven in industry on large scale at high yield, including such companies as Enerkem (38 ML trash-to-methanol plant)

- The second half of this process, taking **acetic acid to ketene to diketene and then to butanols**, has been demonstrated by Pioneer Energy at 10 L/day with CCEMC funding:
    - 70% ketene yield from acetic acid
    - 98% diketene yield from ketene
    - 100% MAA yield from diketene
    - 80% butanol yield from MAA
    - 55% yield, Path forward to improve net yield to > 80%

- **We have performed CO_2 Lifecycle Assessments (LCA) and techno-economic feasibility studies of the process**

Part of 10 L/day scale butanol apparatus

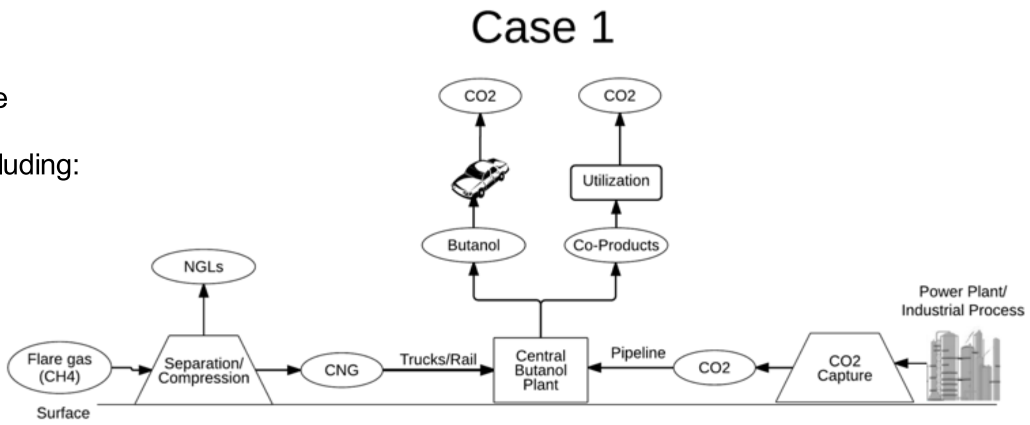


Output from 10 L/day butanol apparatus

CO_2 Lifecycle Study Methodology

- **We used Alberta as a case study, and these results can be easily generalized to other locations**
- **Three cases were studied: Flare gas, natural gas, and landfill biogas for CH_4 source**

- Baseline for existing conditions:
  - Gasoline produced from Average Alberta Oil
  - Flare gas emissions
  - Flue gas (CO_2) emissions from stationary source
- Baseline compared to the LCA system emissions, including:
  - Butanol production
  - Butanol combustion
  - Energy needed for the process comes from Alberta average electricity mix

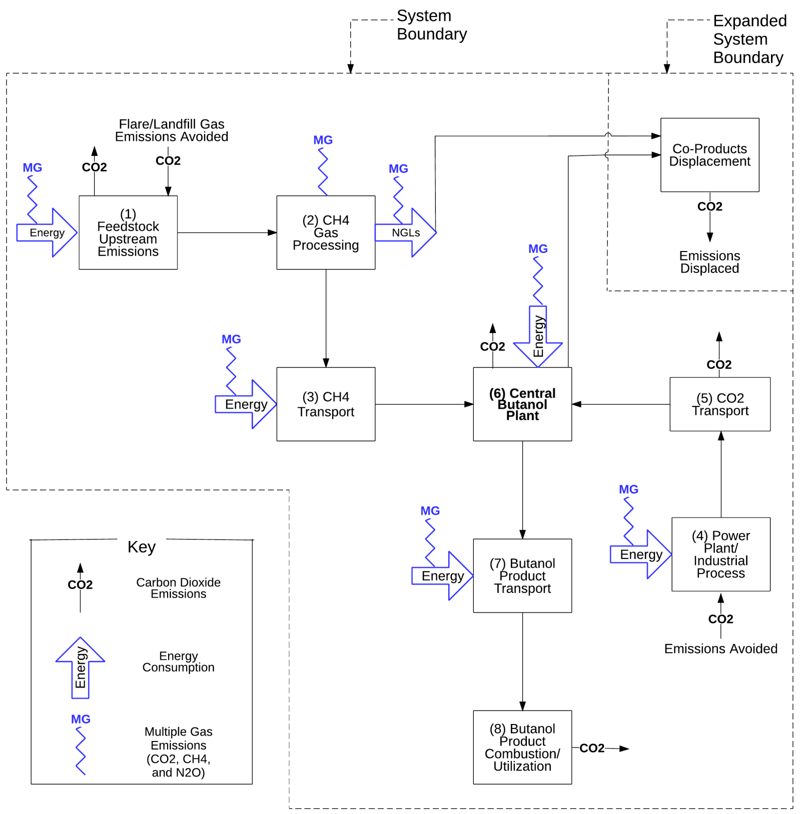


CO_2 LCA System Boundary

Functional Unit: 1 MJ butanol produced (LHV)

The following lifecycle stages were considered in the LCA analysis, following the numbering in the figure:

1. Upstream CH_4 Emissions/Emission Reductions
2. CH_4 Gas Processing
3. CH_4 Transport to Central Butanol Plant
4. CO_2 Capture at Stationary Source
5. CO_2 Transport to Central Butanol Plant
6. Central Butanol Plant Conversion of CH_4 & CO_2 to Butanol
7. Butanol Product Transport
8. Butanol Product Utilization/Combustion



Process Stage 1: Flare Gas Composition, Alberta

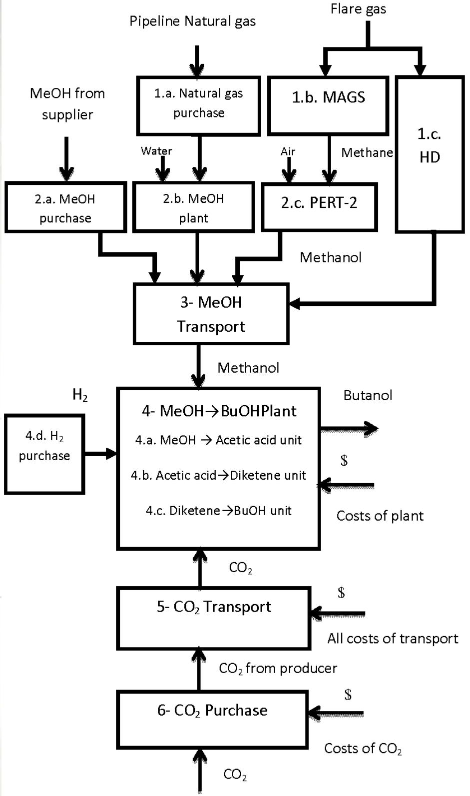
Component	Mole fraction	Mass fraction	Tonne CO_2/ Tonne Flare Gas
C_1 (CH_4)	0.850	0.697	1.912
C_2 (ethane)	0.050	0.077	0.225
C_3 (propane)	0.025	0.056	0.169
iC_4 (iso-butane)	0.005	0.015	0.045
nC_4 (n-butane)	0.010	0.030	0.090
C_5	0.006	0.022	0.067
C_6	0.003	0.013	0.040
C_7^+	0.002	0.010	0.031
N_2	0.030	0.043	
CO_2	0.013	0.028	
H_2S	0.005	0.009	
H_2 & He	~0.0015	~0.0003	
Total CO_2-e			**2.58 ton CO_2-e per ton flare gas**

Source: Johnson, M. R., and Coderre, A. R., **2012**. Compositions and greenhouse gas emission factors of flared and vented gas in the Western Canadian Sedimentary Basin. *J of Air & Waste Management Assoc.*, *62*(9), 992-1002.

Process Stage 2: Flare Gas Capture/Processing

Pioneer Flare gas capture machines, 2 Flarecatcher™ deployed to Bakken flare site, North Dakota, 2015.

Process Stage 6: Central Butanol Plant



Process Flow Diagram

$3CH_4(g) + CO_2(g) = C_4H_{10}O(l) + H_2O$					
Temp	deltaH	deltaS	deltaG	K	Log(K)
°C	kJ/mole	J/K-mole	kJ/mole		
0	-3.6	-510.	136.	1.14E-26	-25.9
25	5.1	-478.	148.	1.30E-26	-25.9
100	12.6	-456.	183.	2.63E-26	-25.6
200	21.2	-435.	227.	8.21E-26	-25.1
300	28.7	-421.	270.	2.46E-25	-24.6
400	36.7	-408.	311.	6.77E-25	-24.2
500	43.0	-399.	352.	1.70E-24	-23.8

Net Process Thermodynamics

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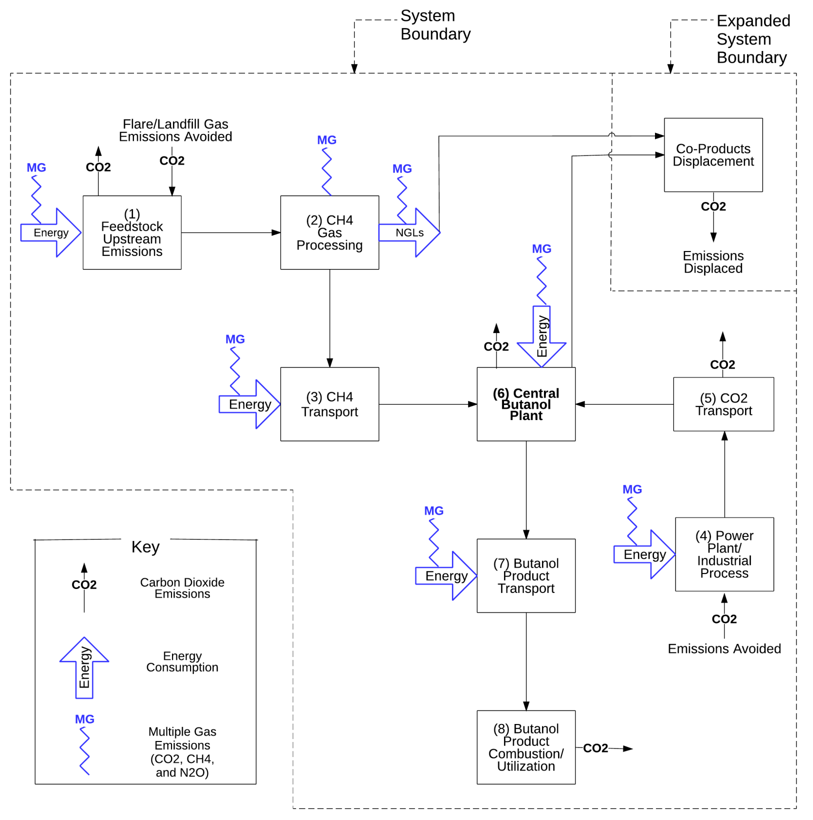
Process Stages 3, 4, 5, 7, and 8

1. Upstream CH_4 Emissions/Emission Reductions
2. CH_4 Gas Processing
3. CH_4 Transport to Central Butanol Plant
   a) Transported as CNG in the conservative case, by combination of truck/rail
   b) Can also be transported as methanol (see other CCUS 2016 talks)
4. CO_2 Capture at Stationary Source
   a) Assume typical 90% CO_2 capture
5. CO_2 Transport to Central Butanol Plant
   a) Assume transport by CO_2 pipelines
6. Central Butanol Plant Conversion of CH4 & CO2 to Butanol
7. Butanol Product Transport
   a) Refined products <1% of process emissions
8. Butanol Product Utilization/Combustion
   a) Displace convention gasoline on 1 MJ-for-MJ basis (LHV)



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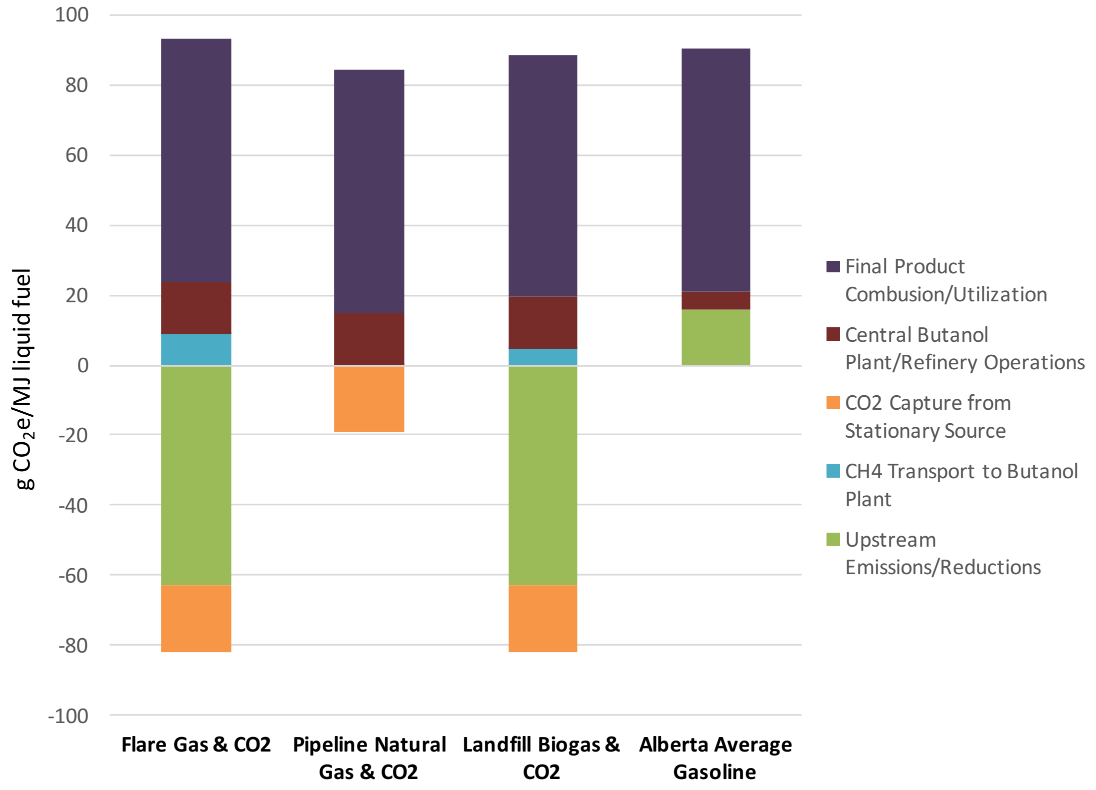
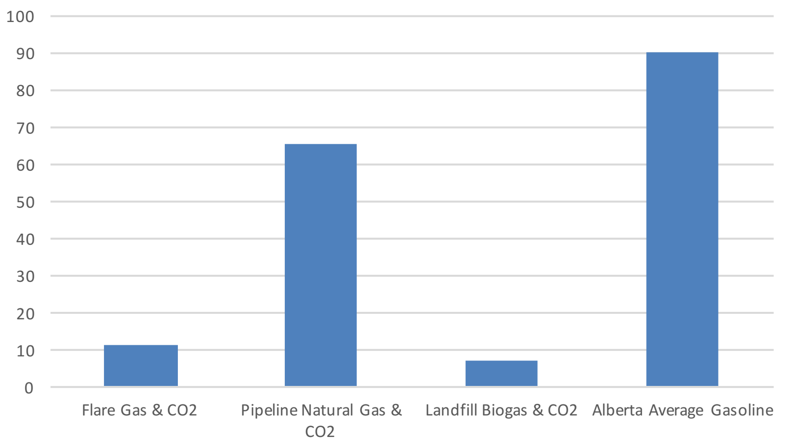
Results – Lifecycle CO_2 Emissions



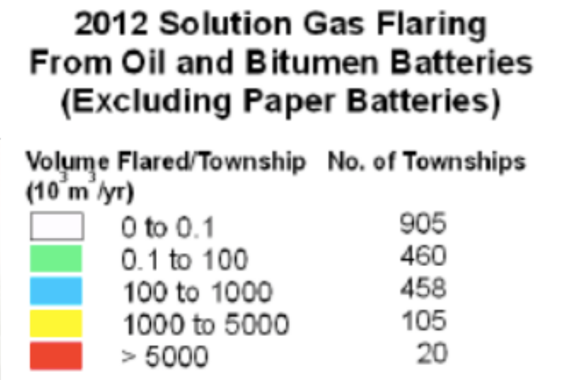


Net Lifecycle Emissions (g CO_2e/MJ liquid fuel)

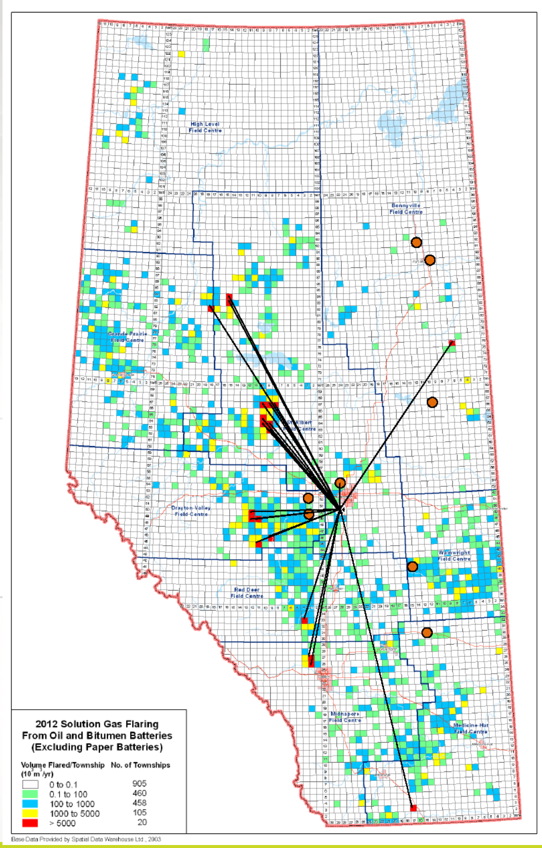
Economic Feasibility (McMaster Study)

Flare gas and CO_2 scenario:

- Flare gas sources, CO_2 sources, and central butanol plant connecting network on flare gas sources map
- Orange circles are CO_2 sources and black circle in the vicinity of Edmonton is the central butanol facility obtained through simulation optimization
- Flare gas density legend:



Source: L. Hoseinzade and T. Adams II. "Supply Chain Optimization of Flare-Gas-To-Butanol Processes in Alberta," *The Canadian Journal of Chemical Engineering*, Manuscript ID CJCE 15-0770.R2 (in press).

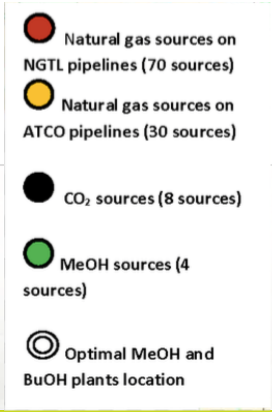


Economic Feasibility (McMaster Study)

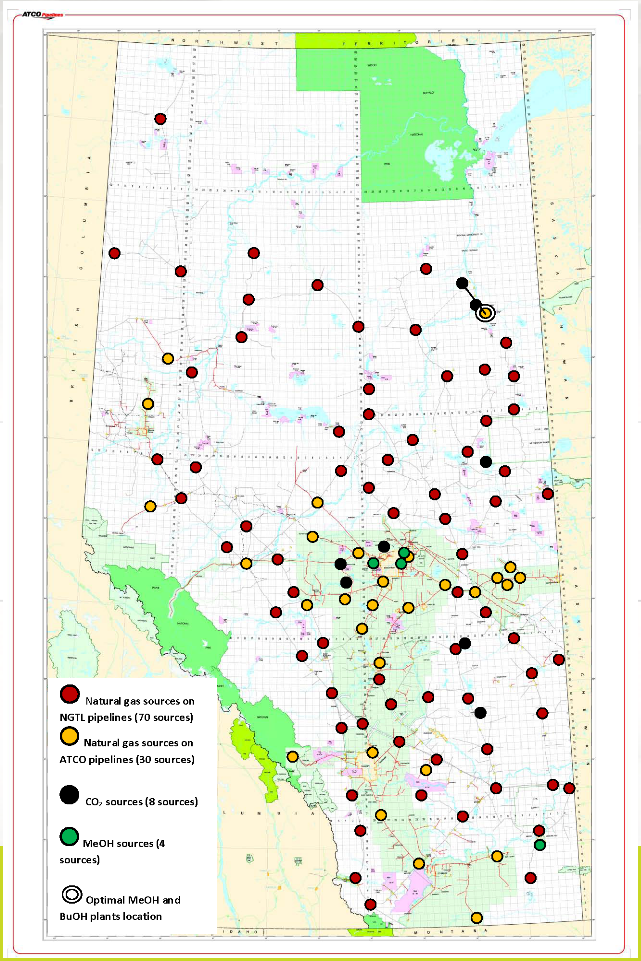
Natural gas and CO_2 scenario:

- 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.

- Legend:



Source: Hoseinzade, L., and Adams, T. A. II. "Supply chain optimization of flare-gas-to-butanol processes in Alberta," *Can J Chem Eng,* 2016, Manuscript ID CJCE 15-0770.R2 (in press).

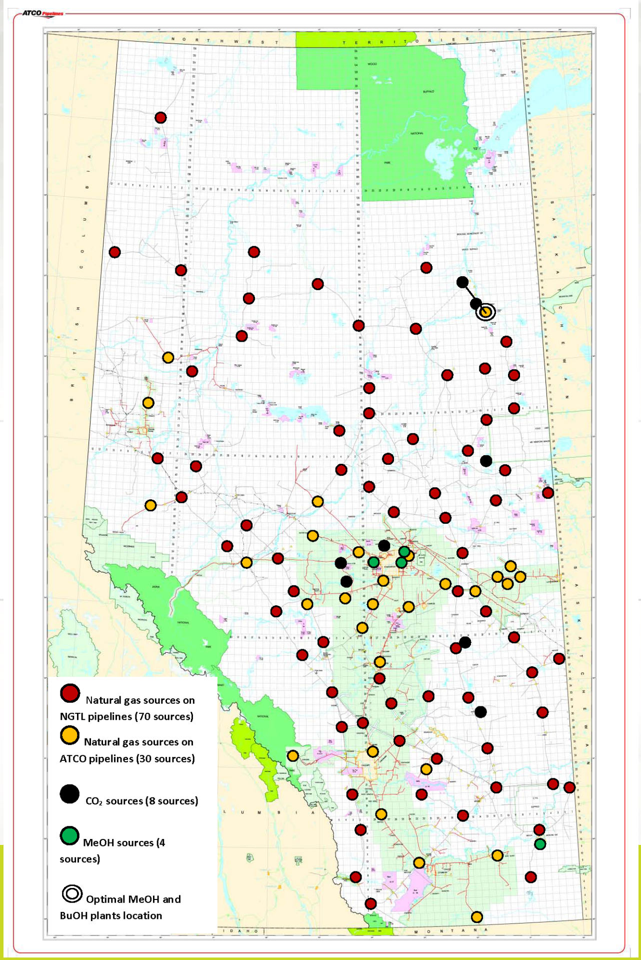


Techno-economic Feasibility Analysis

- **The CO_2 emissions in Alberta could be decreased by about 0.24% by the activity of producing butanol, just from *<u>one</u>* butanol plant utilizing natural gas & CO_2 feedstock.**

- It was found that the process which uses ***natural gas*** & CO_2 from a stationary source is a profitable way of producing butanol while consuming large quantities of CO_2. There are many possible places across Alberta near pipeline connections and CO_2 sources where the process could be located and achieve high profitability.

- By using a combination of ***flare gas,*** pipeline natural gas & CO_2, a system can be designed which is not only profitable, but it also reduces the total CO_2 emissions in Alberta by **0.12% from just *<u>one</u>* butanol plant**.



<u>Source:</u> Hoseinzade, L., and Adams, T. A. II. "Supply chain optimization of flare-gas-to-butanol processes in Alberta," *Can J Chem Eng,* 2016, in press.

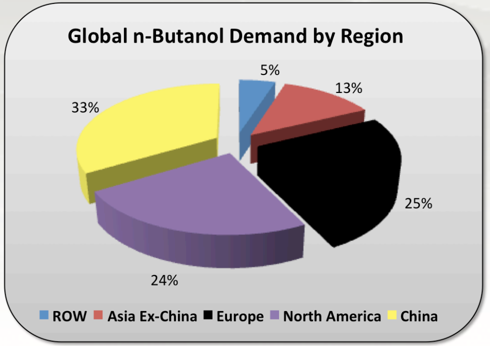
Market for "Green" Chemical Butanol

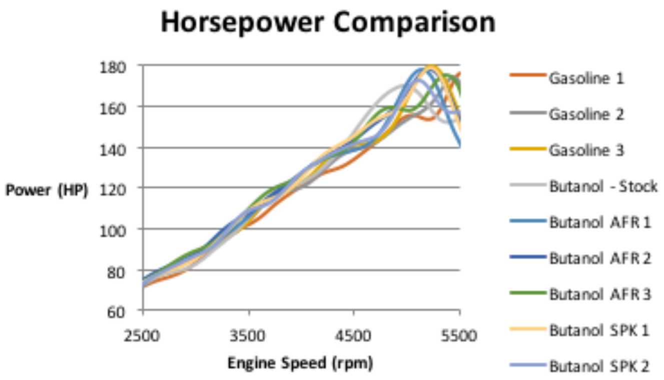
- As a "green" chemical alternative, the market for 1-butanol in the pharmaceutical, chemical, & polymer (butyl acrylate) industries is estimated at over **$5B/year**, *at a value significantly above what its energy-value alone implies*.

- As a gasoline blender or extender, 1- and 2- butanol can access a >$1T per year market.

- We have performed dynamometer tests on mixtures of 50/50 mixtures of 1- and 2- butanol, demonstrating drop-in fuel performance on a *2007 Chevrolet Cobalt with the Ecotec 2.2L*.

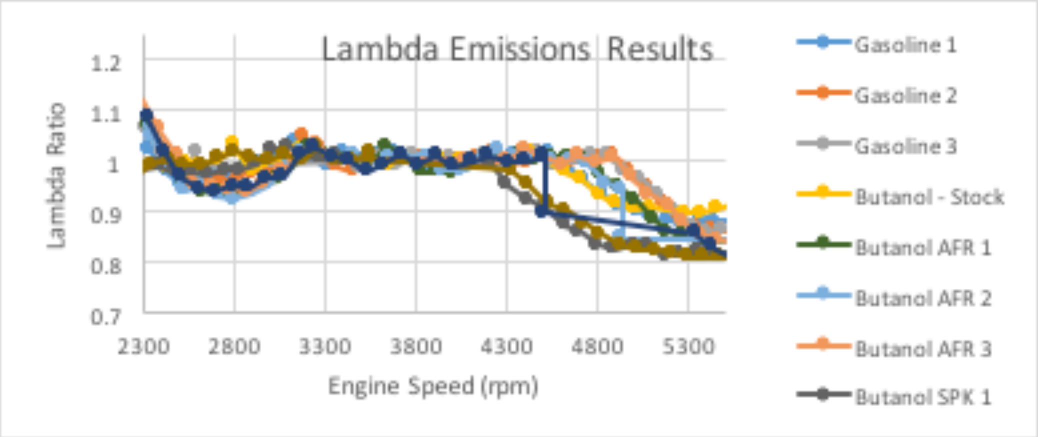
- Automobiles have been driven on 100% butanol across the country, so the 15% legal limit can be raised when butanol production & utilization warrant an increase. Fully compatible with existing distribution pipelines & infrastructure.

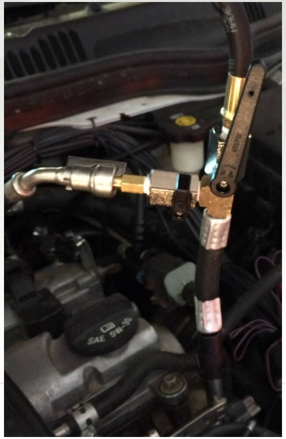


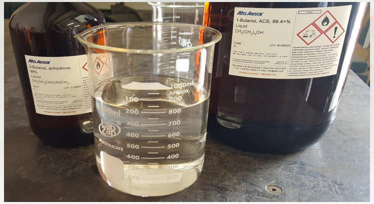


1- and 2- Butanol Mixture Engine Tests

Dynamometer Testing performed – Lambda is a ratio of the hydrocarbon's air to fuel ratio divided into the measured exhaust air to fuel ratio. Any value from .95-1.05 is within normal operating parameters. The dip to 0.8-0.85 during hard acceleration is due to the vehicle entering a power enrichment mode, which causes an injection of extra fuel to maintain safe operating temperatures in the combustion chamber. **All of the test results shown are within expected norms.**

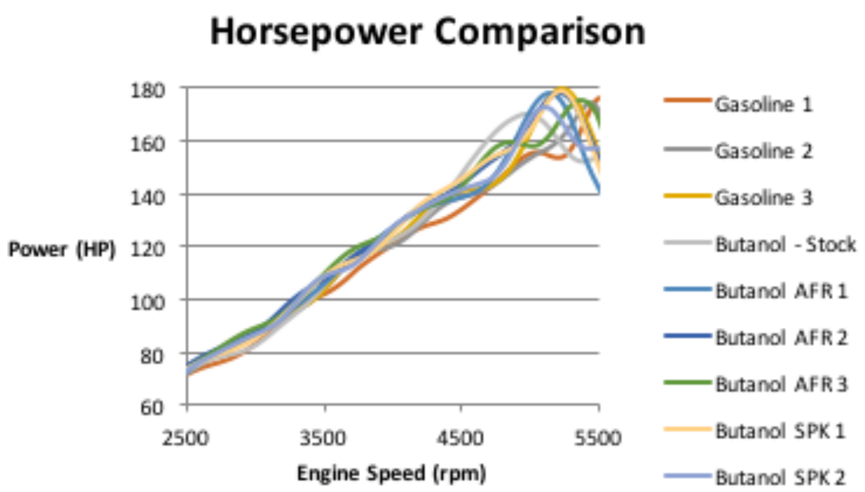


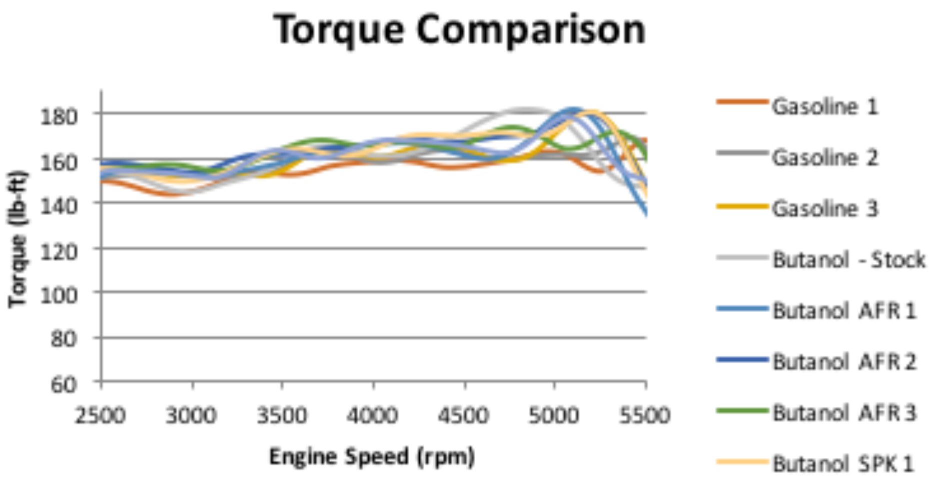

Fuel switch assembly


Butanol Test Fuel


Fuel supply with pressure regulator

1- and 2- Butanol Mixture Engine Tests

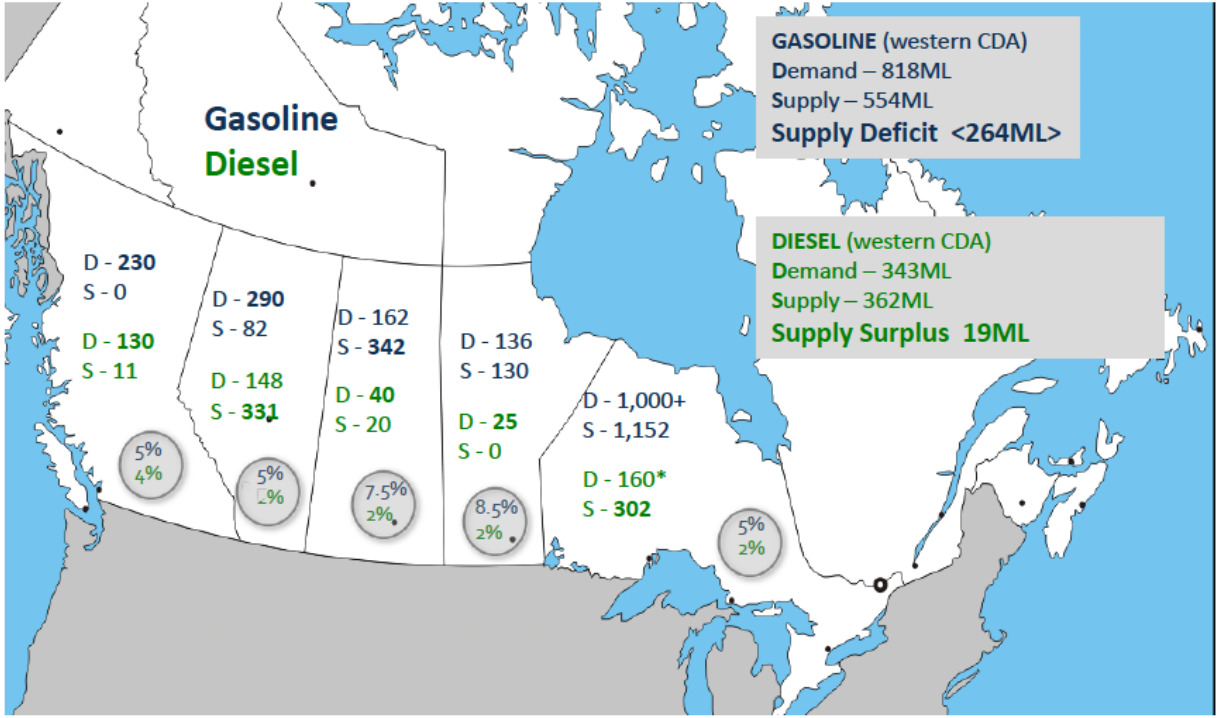




The Dynocom 5000 results indicate the vehicle was able to make the same power or slightly better than gasoline on the butanol blend. This indicates that the fuel can be utilized in not only a flex-fuel vehicle, but also in an unmodified gasoline engine as well.

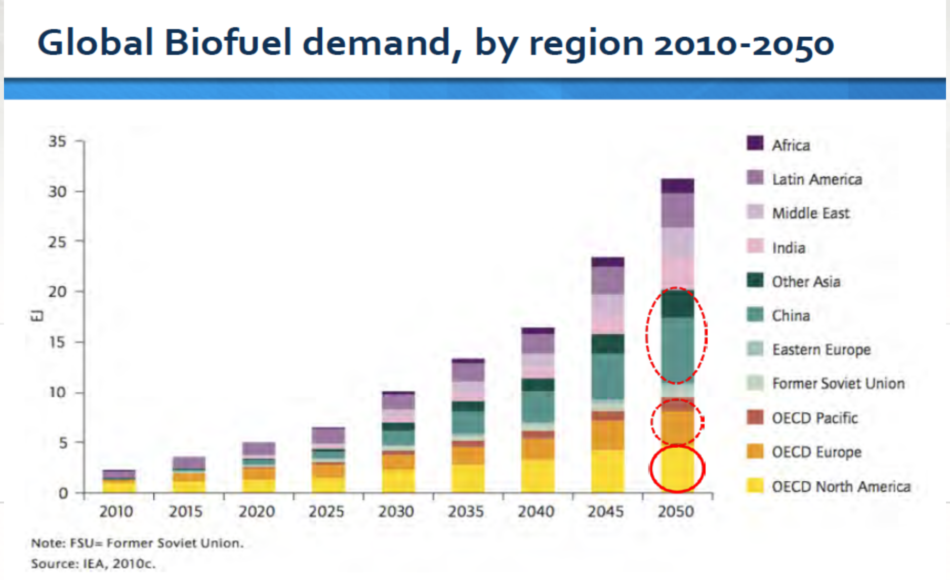
Video available: https://youtu.be/XxC03JbA1Q0

Fuel Market Potential in Canada

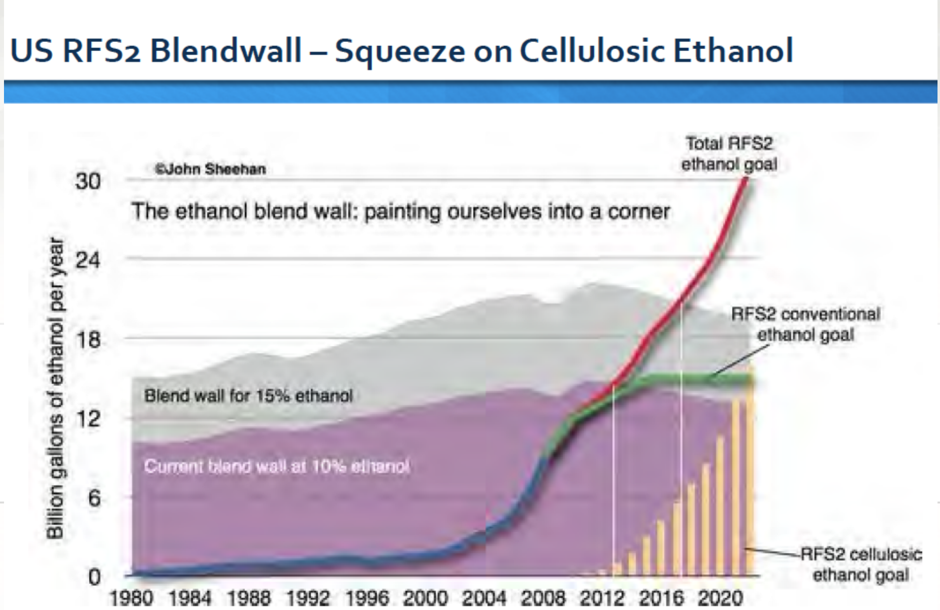


Supply and Demand Differential in Gasoline and Diesel in Canada
(<u>Source:</u> Ian Thomson, Waterfall Group, 2013)

Ethanol Blend Wall Opportunity



Global biofuel demand
(Source: Ian Thomson, Waterfall Group, 2013)



Ethanol blend wall
(Source: Ian Thomson, Waterfall Group, 2013)

Concluding Remarks

- **Butanol from CO_2 turns pollution into fuel**
  - Our technology transforms currently-wasted emissions into a valuable resource
  - Demonstrated conversion with a pilot unit at 10 L/day butanol from CO_2 & CH_4
  - Our process eliminates flaring, while utilizing existing CO_2 emissions
- **Synthetic Butanol**
  - High-value "green" chemical
  - Drop-in automotive fuel, fully compatible with existing pipelines
  - Variants can use trash & cellulosic biomass as feedstock

Thank you to Canada's *Climate Change Emissions Management Corporation (CCEMC)* for funding this work!

Pioneer Energy Background

Founder

- Astronautical engineer
  Dr. Robert Zubrin

Resources

- $30+ million private capital
- $550,000 DOE (RPSEA) grant
- $500,000 Canadian grant
- $2.7M NASA-funded research
- IP portfolio of 30+ issued U.S. patents, 3 in Canada

Product lines

- Field mobile natural gas processing plant
- Field mobile CO_2-EOR systems
- Synthetic fuel technology for butanol and C4+ chemicals/fuels

Team

- 15 engineers, chemists, technicians, and machinists

Partners

McMaster University

CLEMSON UNIVERSITY