# Technologies for Upgrading Landfill Gas to a High-Quality Fuel

John N. Kuhn

USF and T2C-Energy LLC

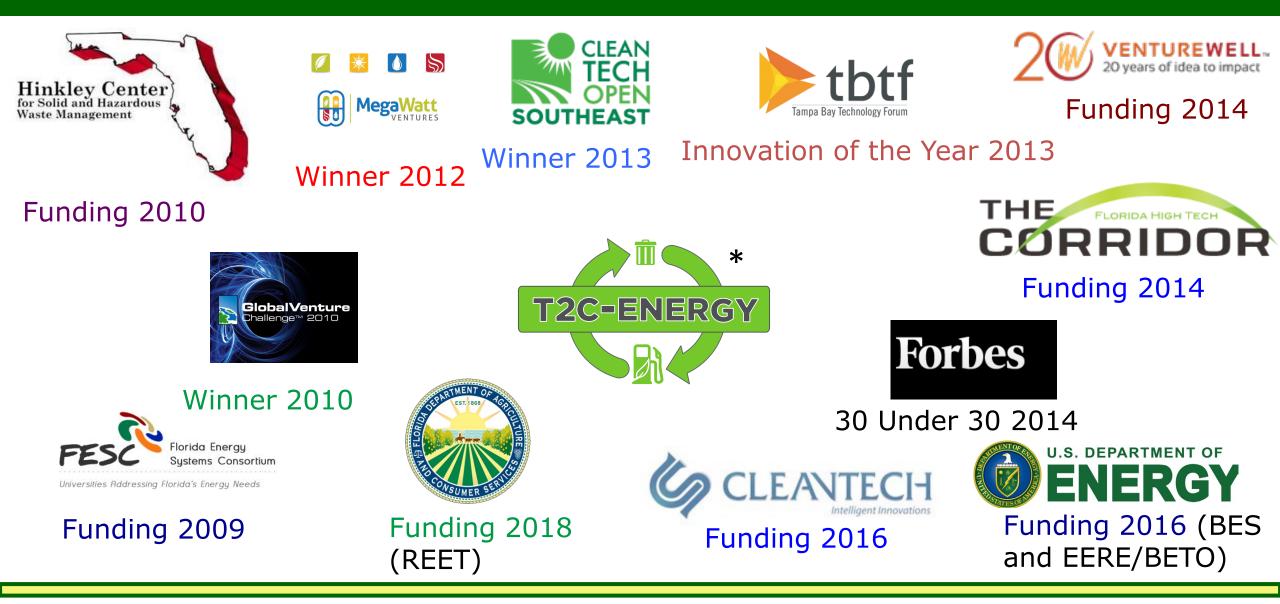
2023 SWANA FL Summer Conference



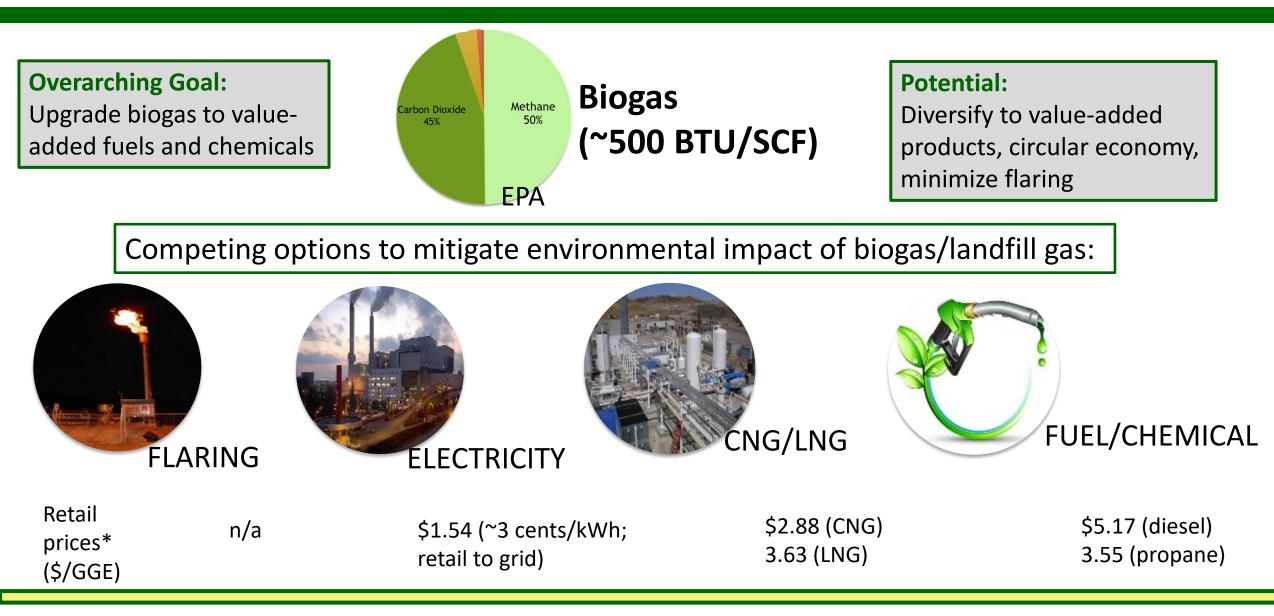


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### ACKNOWLEDGMENTS

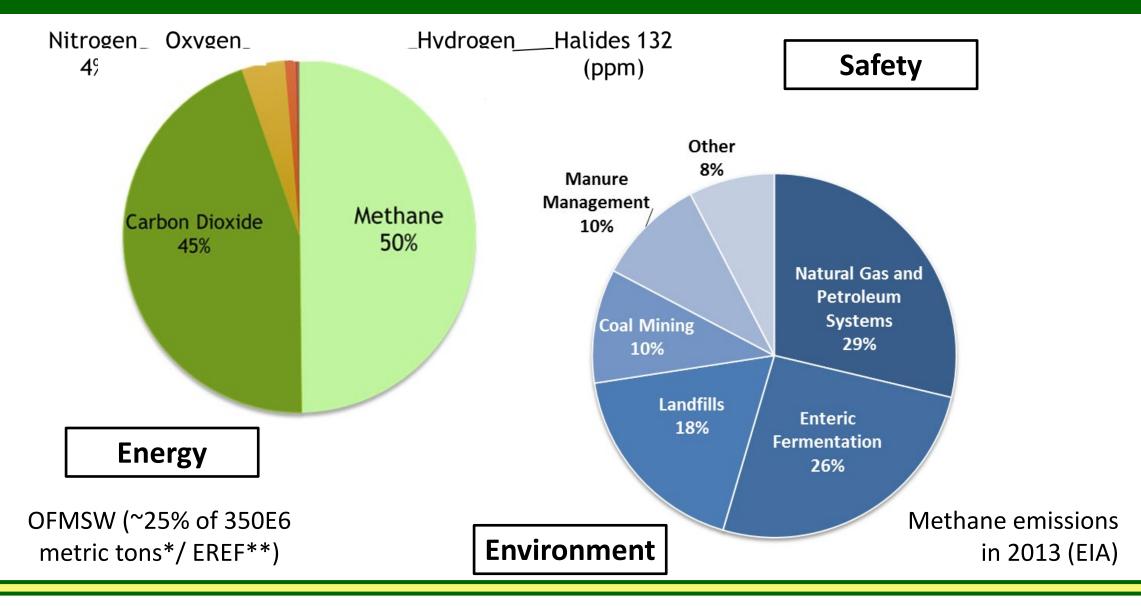


# THE BIG PICTURE



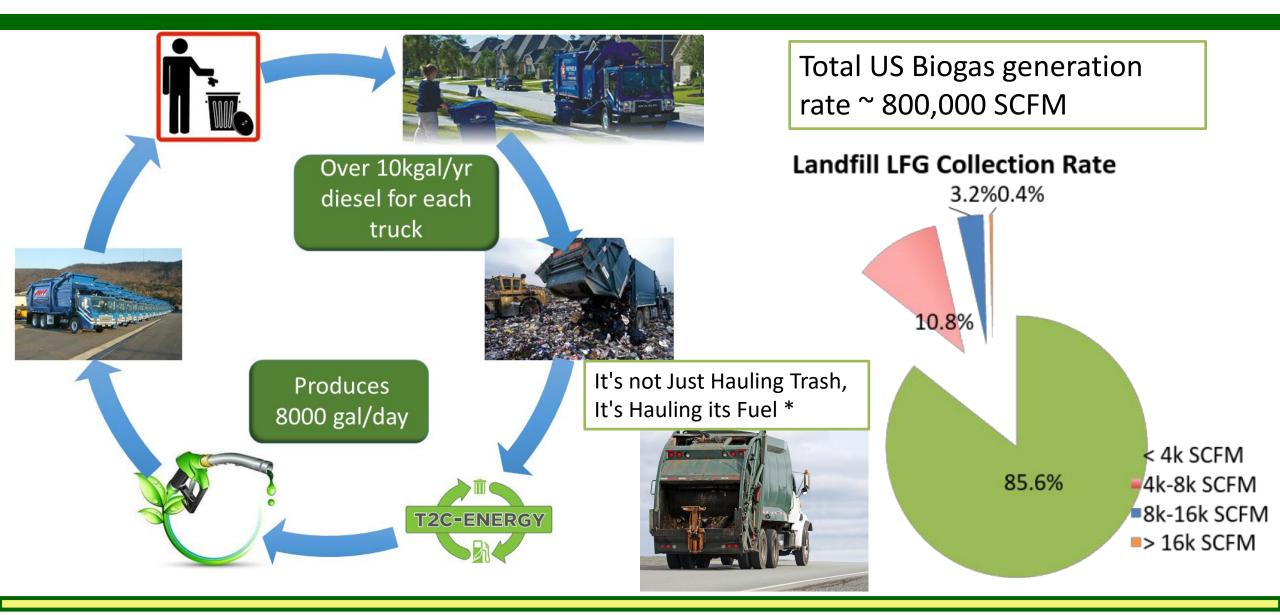
\*Oct. 2022; https://afdc.energy.gov/fuels/prices.html

# **PROBLEM/OPPORTUNITY**



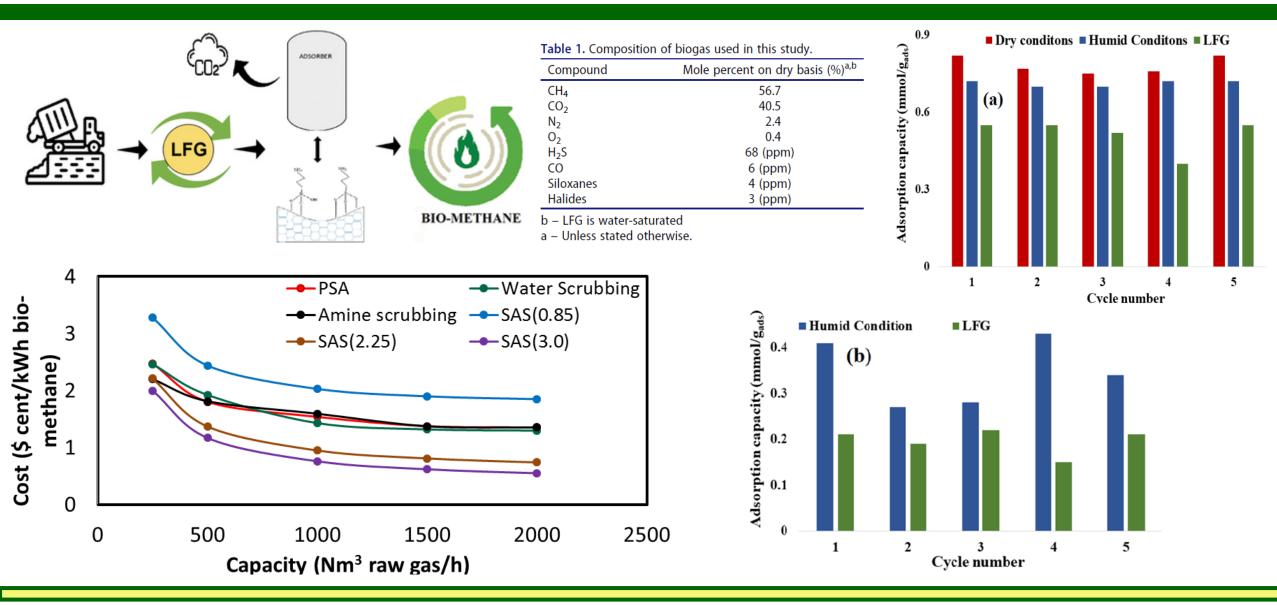
\*another 87E6 tons that is recycled and composted / \*\* 40% higher than EPA

# **PROBLEM/OPPORTUNITY**



\* www.t2cenergy.com

# **RENEWABLE NATURAL GAS**



(PSA, Water scrubbing, and amine scrubbing data from Peterson & Wellinger, 2009)

## **NEED FOR HYDROCARBON FUELS**

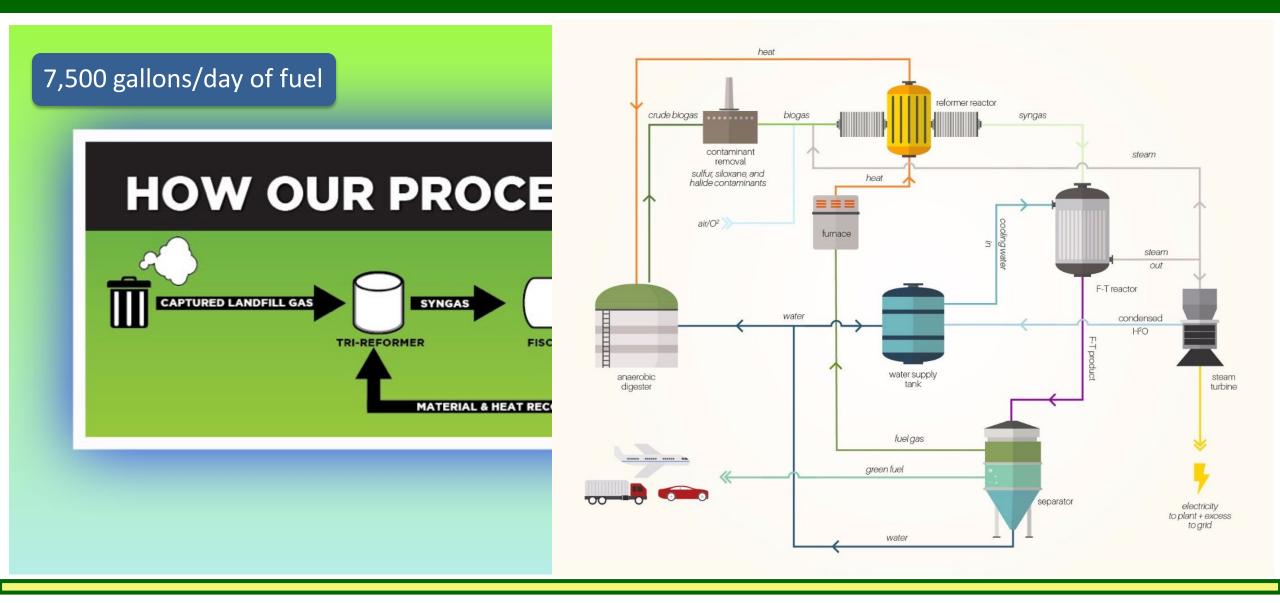
#### **Plastics** \*

- 8300 million metric tons plastics produced to date
- 6300 million metric tons plastics discarded as waste to date
- Of waste, 9% recycled, 12% incinerated, and 79% landfilled
- 12,000 million metric tons anticipated by 2050 (landfilled or in environment)
- Only 4 million metric tons of bio-based biodegradable
- ~13 % of U.S. MSW is plastics in 2013 (before recycling)\*\*

#### Energy-Dense Liquid Hydrocarbon Fuels (i.e., Diesel)

- 100 million bbl crude oil used worldwide per day (~25% in U.S.)
- Equates to 4500 million metric tons per year
- Need for diesel expected to increase
- Waste industry represents 4% of US diesel consumption
- Diesel and jet fuel harder to replace than gasoline

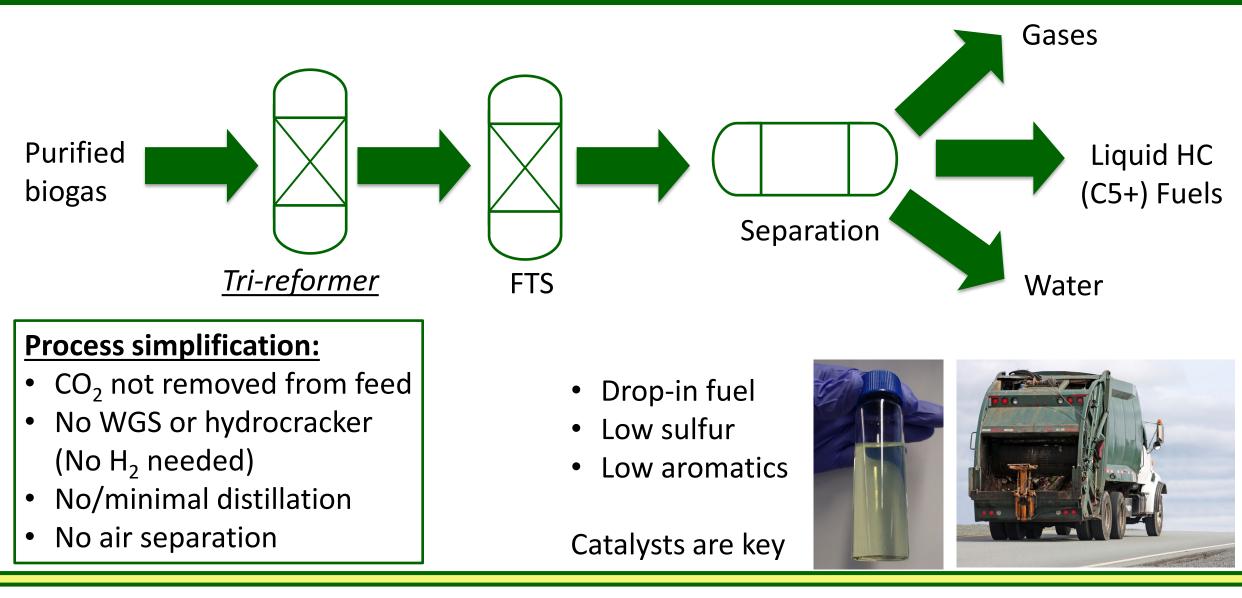
# **TRIFTS<sup>TM</sup> PROCESS OVERVIEW\***



\* Patent approved

#### www.t2cenergy.com

# **TRIFTS PROCESS OVERVIEW\***



# LAB/BENCH SCALE TRIFTS<sup>TM</sup> UNIT



#### **Microreactor**

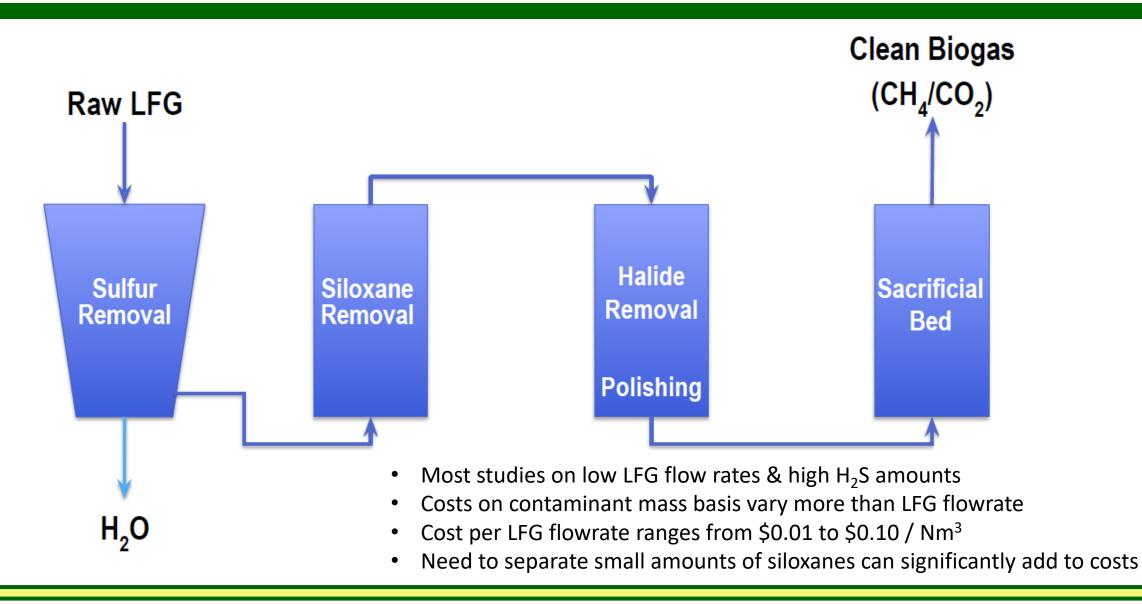
- 100 mg ref. catalyst
- < 100 SCCM
- Powder catalyst
- Low Pressure
- No MTL/HTL

#### **Bench Scale\***

- ~ 3 g ref. catalyst
  - 1-3 sLPM
  - Pellet catalyst
- Pressure < 30 bar</li>
  - MTL/HTL ?



### **PURIFICATION TRAIN**



# **LFG CONTAMINANTS**

Siloxanes				NMOCs		
Hexamethyldisiloxane[L2]: $(C_6H_{18}OSi_2)$	162	0.38-5.0	Isopropyltoluene: (C <sub>10</sub> H <sub>14</sub> )	134.2	48.8-73.6	
Octamethyltrisiloxane[L3]: (C <sub>8</sub> H <sub>24</sub> O <sub>2</sub> Si <sub>3</sub> )	236	0.23-0.05				
Decamethyltetrasiloxane[L4]: (C <sub>10</sub> H <sub>30</sub> O <sub>3</sub> Si <sub>4</sub> )	310	0.005-0.1	$\alpha$ -pinene: (C <sub>10</sub> H <sub>16</sub> )	136.2	4.4-85.3	
Hexamethylcyclotrisiloxane [D3]: (C <sub>6</sub> H <sub>18</sub> O <sub>3</sub> Si <sub>3</sub> )	222	0.01-0.84	Camphene: (C <sub>10</sub> H <sub>16</sub> )	136.2	1.5-5.4	
Octamethylcyclotetrasiloxane [D4]: (C <sub>8</sub> H <sub>28</sub> O <sub>4</sub> Si <sub>4</sub> )	297	1.083-15.0	Limonene: (C <sub>10</sub> H <sub>16</sub> )	136.2	15.8-52.9	
Decamethylcyclopentasiloxane [D5]: (CHO-Si-)	371	0.40-1.135	Terpinene: (C <sub>10</sub> H <sub>16</sub> )	136.2	3.4-10.7	
Sulfur			Octane: (C <sub>8</sub> H <sub>18</sub> )	114.2	3.5-6.0	
Hydrogen Sulfide: (H <sub>2</sub> S)	34.1	99.9-280	Nonane: (C <sub>9</sub> H <sub>20</sub> )	128.2	14.9-18.3	
Methanethiol: (CH.S)	48.1	0.56	Decane: (C <sub>10</sub> H <sub>22</sub> )	142.3	18.0-27.9	
Halides			Undecane: (C <sub>11</sub> H <sub>24</sub> )	156.3	8.5-16.2	
(-2-4)			Dodecane: (C <sub>12</sub> H <sub>26</sub> )	170.3	0.6-1.8	
CarbonTetrachloride (CCl <sub>4</sub> )	154	41.5-124.3 pp	Hexadecane: (C <sub>160</sub> H <sub>34</sub> )	226.4	<0.10	
Chloroform (CHCl <sub>3</sub> )	113	78.6-183.9 pp	Benzene: (C <sub>6</sub> H <sub>6</sub> )	78.1	0.85-4.7	
Trichloroethene (C <sub>2</sub> HCl <sub>3</sub> )	131	0.9-2.6	Isopropylbenzene: (C <sub>9</sub> H <sub>12</sub> )	120.2	3.3-5.6	
Tetrachloroethene: (C <sub>2</sub> Cl <sub>4</sub> )	165.8	0.14-0.30	Xylenes: (C <sub>8</sub> H <sub>10</sub> )	106.2	35.6-74.1	
Chlorobenzene: (C <sub>6</sub> H <sub>5</sub> Cl)	112.6	0.22	Toluene: (C <sub>7</sub> H <sub>8</sub> )	92.1	4.96-37.2	
Mercury						
MonomethylMercury (CH <sub>3</sub> Hg)	216	1-47ng/m <sup>3</sup>	DimethylMercury (CH <sub>3</sub> ) <sub>2</sub> Hg	231	2.1-91 ng/m³	

## **SULFUR REMOVAL PROCESSES**

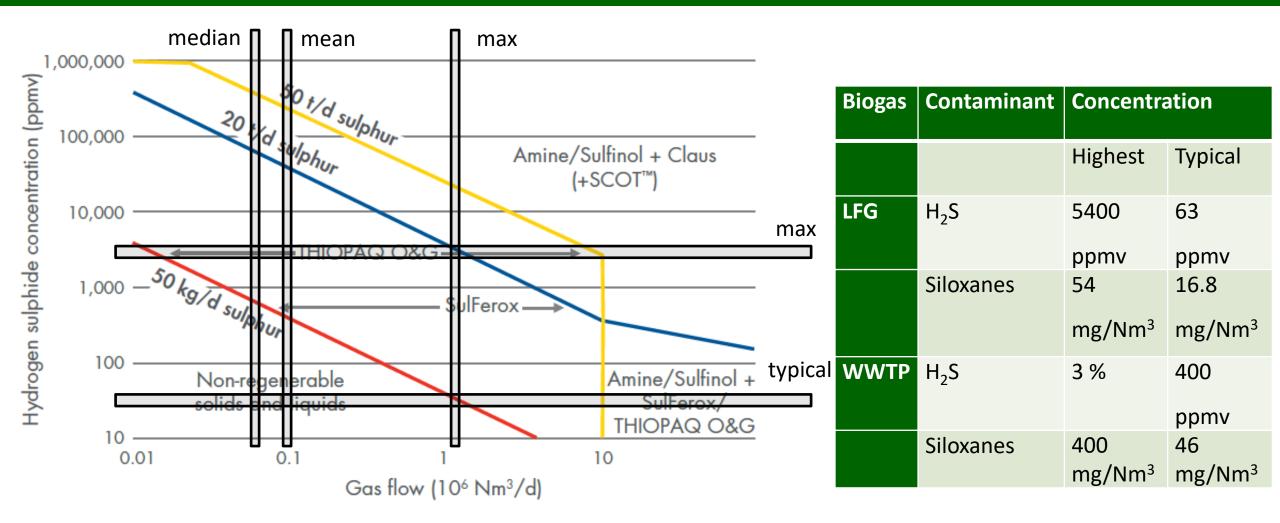
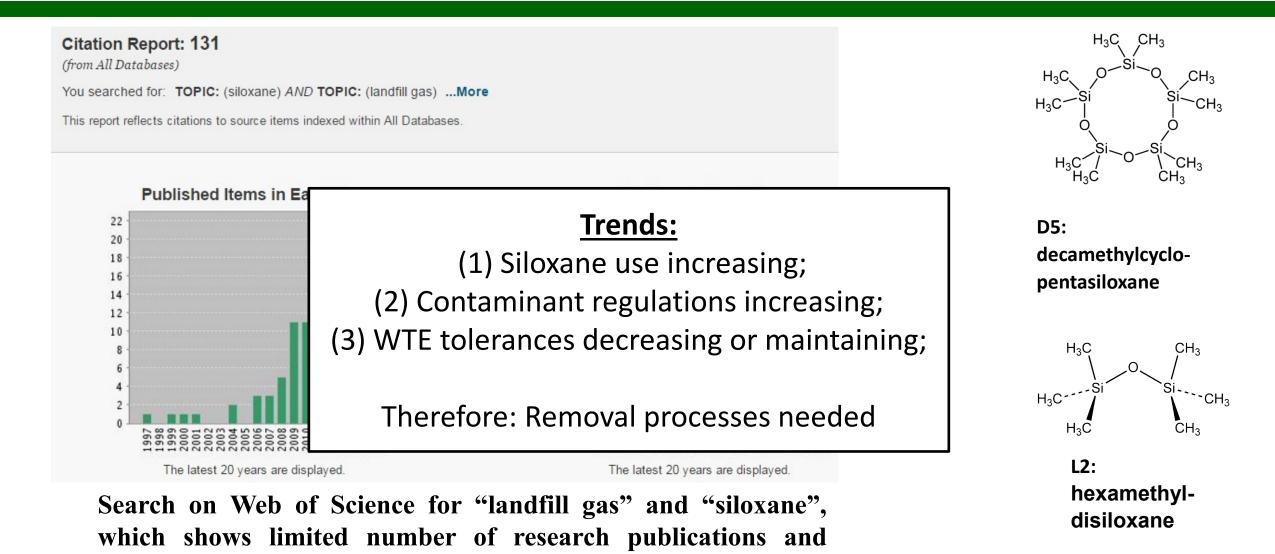


Figure 1: Hydrogen sulphide processing selection chart.

### **SILOXANES**



citations and an exponential increase in these efforts.

# SILOXANES (ACCELERATED TESTING)

Sample	Nomenclature	Theoretical	Actual Mass	% error	
Sample		Mass gain SiO <sub>2</sub>	Gain SiO <sub>2</sub>	<i>7</i> 8 error	
1 week NiMg	1W-NiMg	2.6%	1.5%	-43.5%	
1 month NiMg	1M-NiMg	11.1%	11.9%	7.5%	
6 month NiMg	6M-NiMg	66.7%	65.7%	-1.5%	Fresh Catalyst
1week Pt	1W-Pt	2.6%	1.1%	-59.4%	
1 month Pt	1M-Pt	11.1%	10.5%	-5.4%	CONTRACT RECOVER TO A THE REAL OF
6 month Pt	6M-Pt	66.7%	61.9%	-7.2%	the second secon

#### 6 month poisoned

# SILOXANES (ACCELERATED TESTING)

Pt Catalysts	-	nversion ature (°C)	CO <sub>2</sub> Conversion (°C		H₂:CO (@450°C)
	X <sub>10</sub>	X <sub>50</sub>	X <sub>10</sub>	X <sub>50</sub>	
Fresh*	454	603	432	578	0.30
1W-Pt	518	630	503	613	0.22
1M-Pt	535	675	510	657	0.20
6M-Pt	587	752	566	726	0.11
	CH <sub>4</sub> Co	nversion	CO <sub>2</sub> Conversion Temperature		H <sub>2</sub> :CO
NiMg Catalysts	Temper	ature (°C)	[°C	2)	(@ <sup>8</sup> 00°C)
	X <sub>10</sub>	X <sub>50</sub>	X <sub>10</sub>	X <sub>50</sub>	
Fresh	760	040	740	010	0.31
	762	848	742	813	0.51
1W-NiMg	810	848 900	742	813	0.31

Conversions for methane dry reforming -nr: Not reached n/a: not applicable since there was no reactant conversion

\* Based on speculation that performance 1 week samples may be acceptable

Most siloxanes

need removed

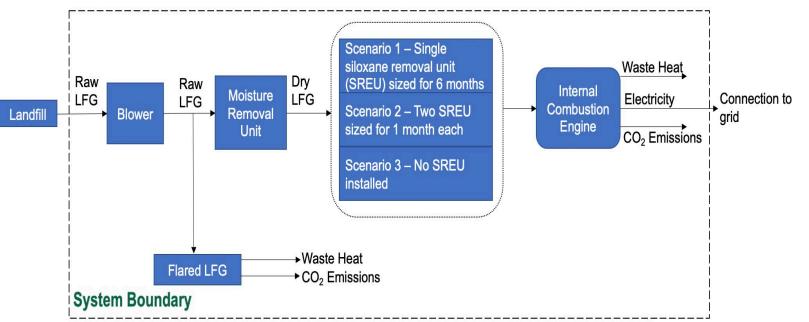
(≥96%\*)

 $5 \text{ mg/m}^3$ 

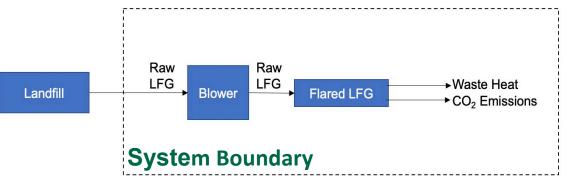
fed

≤0.2 mg

# SILOXANE REMOVAL FROM LFG



- Four Scenarios studied.
- 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> scenarios generated electricity.
- 4<sup>th</sup> scenario flared LFG.



Facility that flares all LFG captured (Scenario 4).

removal units.

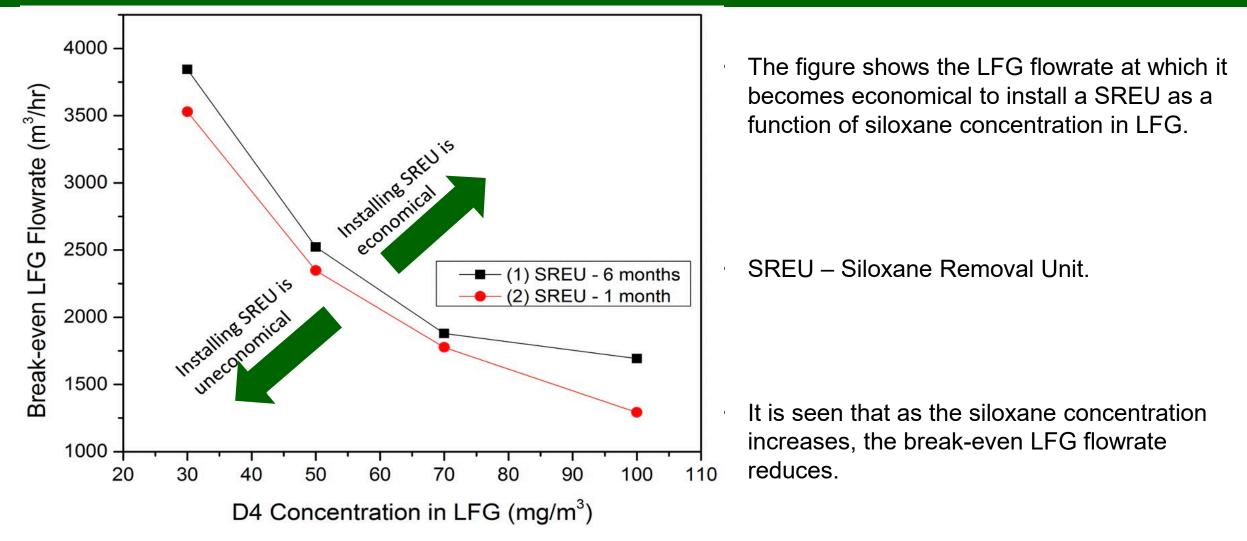
unit.

Facilities that generates electricity (Scenarios 1 - 3)

•

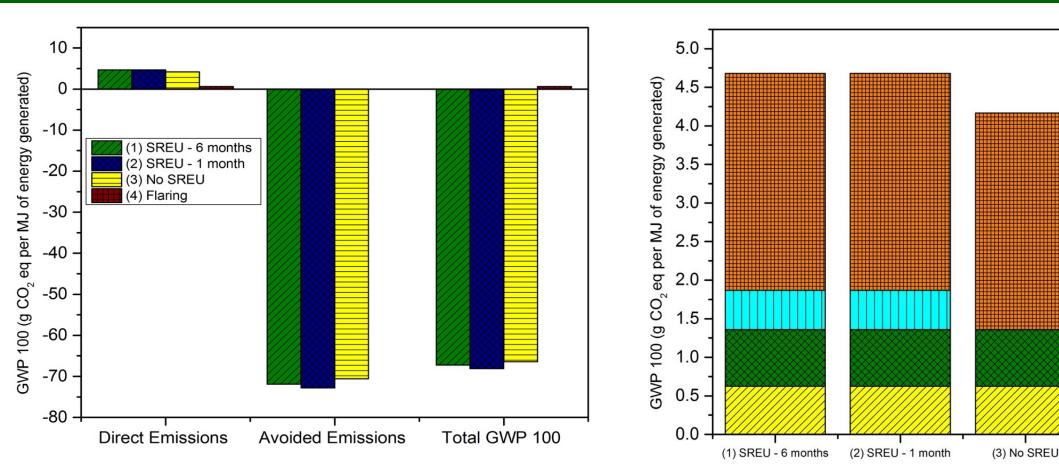
1<sup>st and</sup> 2<sup>nd</sup> scenarios installed siloxane

### **TEA RESULTS**



Effect of D4 concentration and biogas flowrate on the annual net cash income.

# **LCA Results**



Comparison of Direct, Avoided and Total Emissions in terms of GWP 100 among the four scenarios (Base case: 1700 m<sup>3</sup>/hr. LFG (50% CH<sub>4</sub>), 50 mg/m<sup>3</sup> D<sub>4</sub>).

GWP 100 of the LFG blower/treatment system and ICE for the four scenarios (Base case: 1700 m<sup>3</sup>/hr. LFG (50% CH<sub>4</sub>), 50 mg/m<sup>3</sup> D<sub>4</sub>).

#### Amaraibi et al, J Env Manage 2021

(4) Flaring

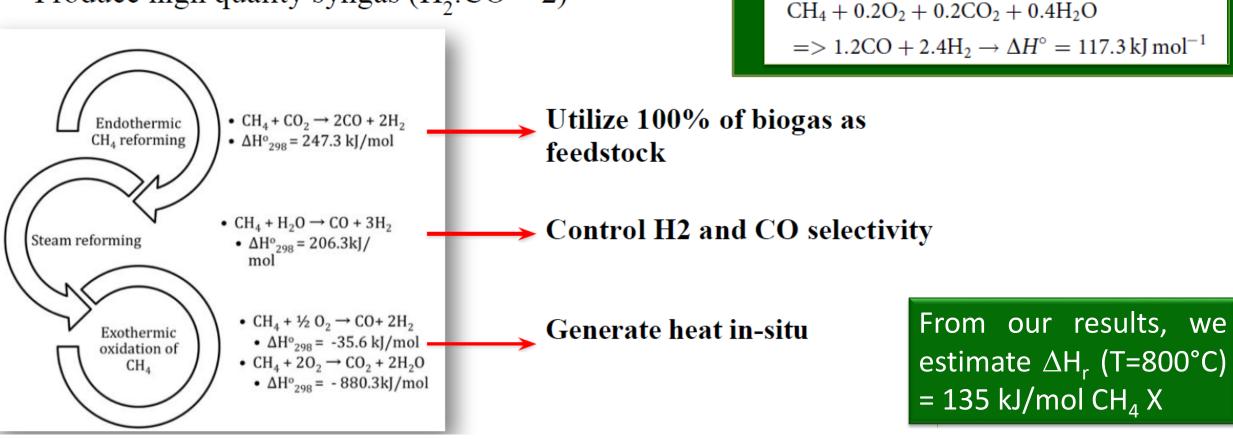
ICE SREU

Chiller

Blower

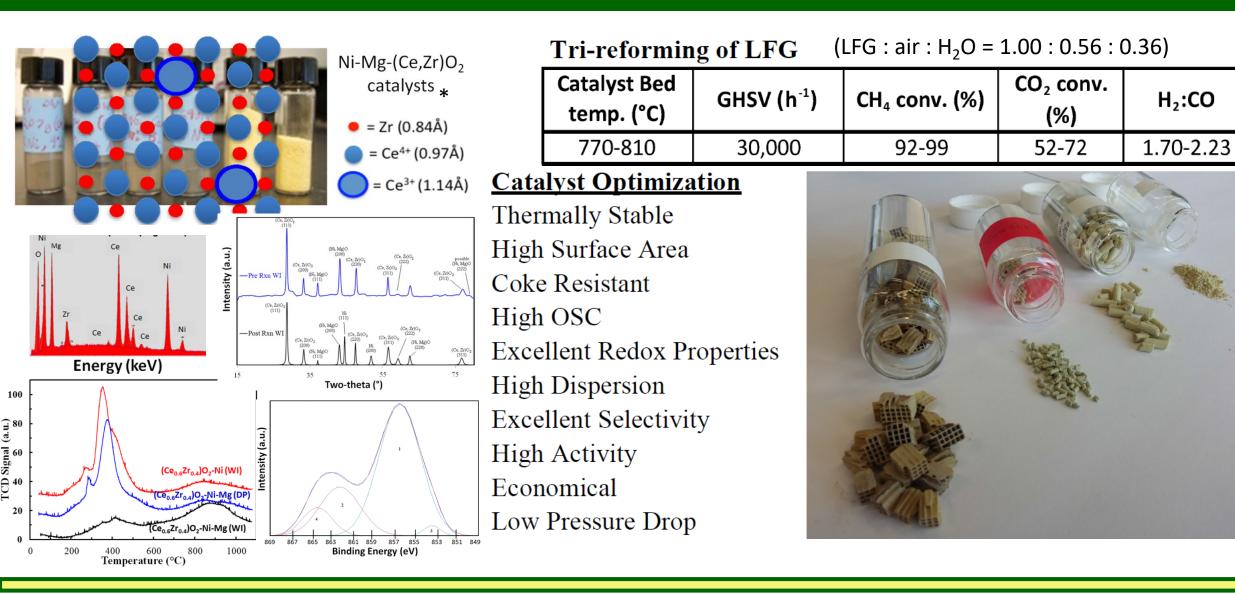
# **CATALYTIC TRI-REFORMING**

- Minimize cleanup and pretreatment process (No CO<sub>2</sub> removal)
- Less energy consumption
- Produce high quality syngas ( $H_2:CO \sim 2$ )



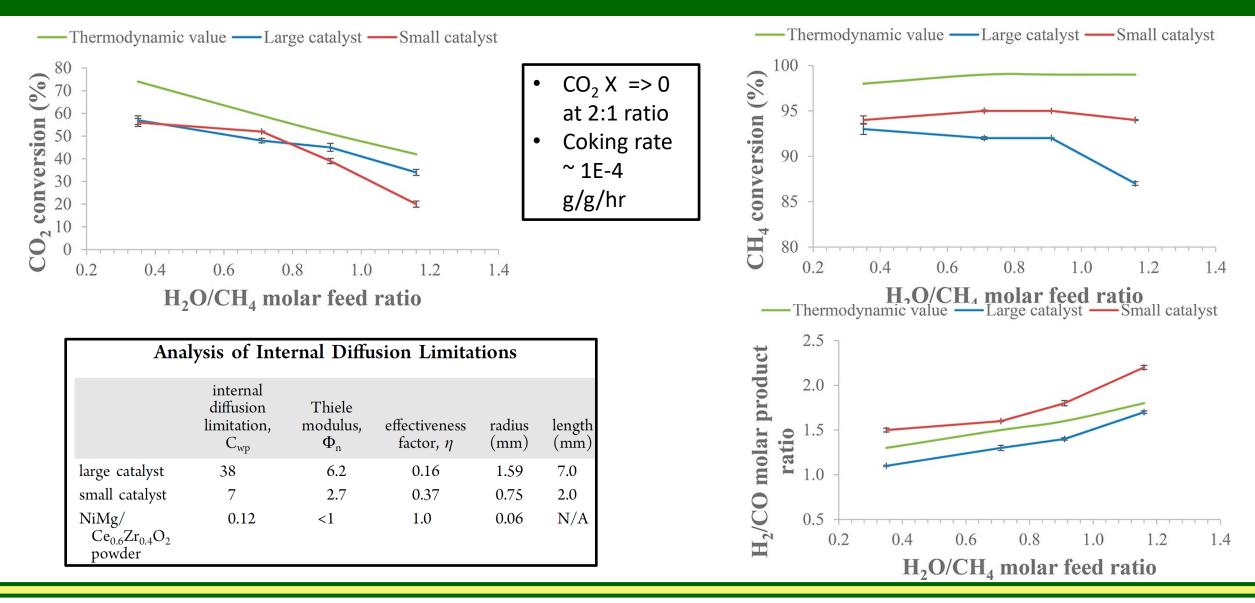
**Global reaction (within constraints)** 

# **CATALYTIC TRI-REFORMING**



\* Powders: Walker et al Appl Catal A:Gen 2012; Pellets: Zhao et al IECR 2018 and Powder Tech 2019

# COMPETITION OF $CO_2 \& H_2O$



Zhao et al, IECR 2019

 $P = 3 \text{ bar}, T = 882^{\circ}\text{C}, CH_4 / CO_2 = 1.4$ 

# **REAL LFG**

Conditions	Feed (CH <sub>4</sub> :CO <sub>2</sub> :H <sub>2</sub> O:air by mole)	CH <sub>4</sub> X (%)	CO <sub>2</sub> X (%)	H <sub>2</sub> :CO ratio
*, 3 bar, ~30k h <sup>-1</sup>	LFG + air + steam*	92-99	52-72	1.7-2.2
882 °C, 3 bar, ~26k h <sup>-1</sup>	1: 0.7: 1.16: 0.95	87	34	1.7
Control: powder (800 °C, 1 bar, 61k h <sup>-1</sup> )	1: 0.7: 0.23: 0.2 (O <sub>2</sub> )	97	78	2.1



\* Temperature and steam added varied, LFG purified, raw LFG ~ 56% methane and 40% CO<sub>2</sub>

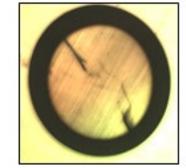
# **CO-BASED FTS CATALYST**

# **FTS Eggshell Catalyst**

- Overcome mass and heat transfer limitations
- Selective product distribution in middle distillate region
- Avoid wax production

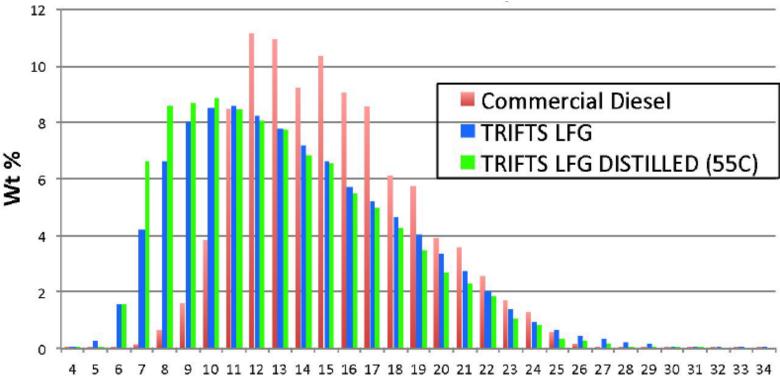
	LFG Energy Recovery	Selectivity (%)			
CO % Conv	In Liq Fuel (%)	<b>C</b> <sub>1-4</sub>	CO <sub>2</sub>	C <sub>5+</sub>	
71	40	43.7	1.4	55.0	





# **FUEL ANALYSIS**

- Low aromatics improve net heat of combustion and reduce soot
- Isomers improve cold temp properties
- Further reduce olefin content w/ addition of catalyst promoters
- Excellent middle distillate boiling point distribution
- Control phase separation temp to fractionate light ends
- Final boiling point aligns with commercial diesel



Carbon #

HC Family/Diesel	TriFTS	Commercial
P - I - O	99.7%	53%
Cyclics (+A)	0.3%	47%

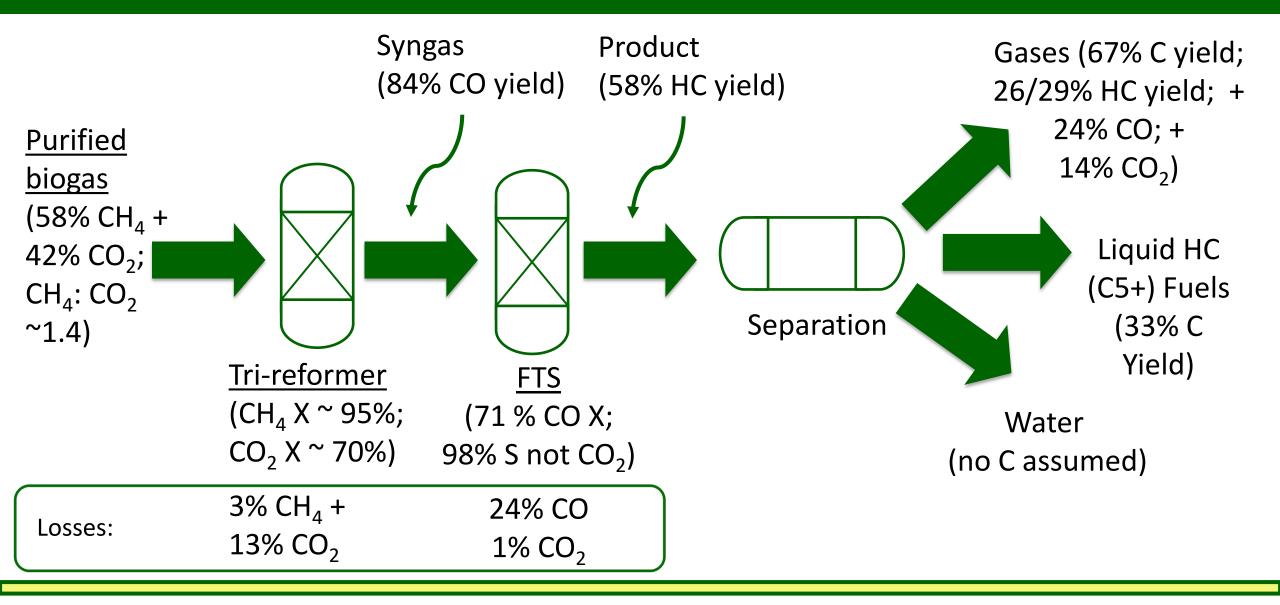
### **FUEL ANALYSIS**

# ASTM D975 "Standard Specification for Diesel Fuel Oils"

#### **Fuel Analysis Results**

Fuel Analysis, ASTM Standard	Spec (No. 2 Diesel)	<b>Commercial Diesel</b>	TRIFTS LFG	TRIFTS LFG (Dist 55C)
Specific Gravity, ASTM D4052 (g/cc)		0.8215	0.7386	0.7489
Cetane Index, ASTM D976	≥ 40	57.6	84.5	72.7
Cetane Index, ASTM D4737	≥ 40	59.7	92.3	83.4
Flash Point, ASTM D93 (°C)	≥ 52	87	49	57
Cloud Point, ASTM D2500 (°C)		-6	-6	-3
Pour Point, ASTM D97 (°C)		-9	-9	-6
Distillation, ASTM D86 (°C)				
IBP: 0.5wt%		203	143	142
10%		220	164	<b>15</b> 4
50%		269	234	216
<del>9</del> 0%	282-338	329	327	314
FBP: 99.5%		378	388	378
Net Heat Comb., ASTM D3338 (MJ/kg)		<b>43.1</b> 64	44.520	44.355

# **TRIFTS PROCESS OVERVIEW\***



\* Neglecting purification train here (material losses minimal; energy losses vary)

# PILOT SCALE (THE DREAM ~ 2013)



# PILOT SCALE (THE PLAN 2017-18)



# PILOT SCALE (THE FIRST TEST SITE 2019)









# PILOT SCALE (CITRUS COUNTY 2019-20)



# PILOT SCALE (PINELLAS COUNTY 2021)

South Cross Bayou Advanced Water Reclamation Facility (AWRF): *Environmental Commitment through Resource Recovery* 



Image: https://www.pinellascounty. org/utilities/south-cross.htm

First biogas from WWTP test Oct. 2021



### MAJOR DOE MILESTONE: 2022

#### Department of Energy's Bioenergy Office Achieves Major Biofuel Technology and Production Milestone

#### JULY 26, 2022

#### Bioenergy Technologies Office »

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Department of Energy's Bioenergy Office Achieves Major Biofuel Technology and Production Milestone



Author: Josh Messner, Technology Manager, Systems The U.S. Department of Energy Bioenergy Technologies Office (BETO) has achieved a significant milestone in decreasing the minimum fuel selling price (MFSP) of drop-in biofuels, which are fuels made from biomass and other waste carbon sources, and that are compatible with existing petroleum fuel infrastructure and conventional vehicles. BETO partnered with T2C-Energy, LLC (T2C) to validate pilot-scale production of drop-in biofuels with a price of \$3 per gallon of gas equivalent (GGE) and at least 60% lower greenhouse gas emissions than petroleum, using T2C's TRIFTS<sup>®</sup> process.

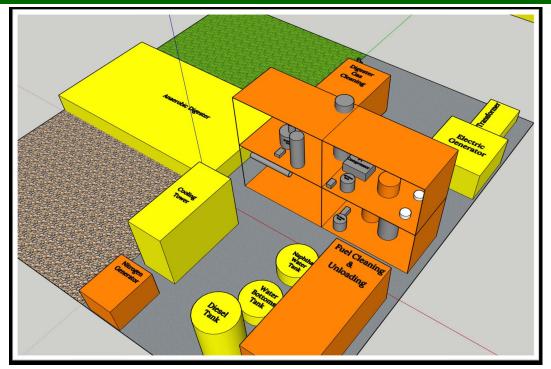
# WHAT'S NEXT?! 2 DOE AWARDS FOR FULL SCALE

Project Title: Demonstration Scale-up: TRIFTS Biogas to Renewable Fuel Lead Organization: T2C-Energy, LLC Principal Investigator: Devin Walker

T2C-Energy developed and patented a proprietary process, we have trademarked TRIFTS<sup>®</sup>, by which to convert biogas (or landfill gas) to liquid transportation fuels. This project seeks to scale the TRIFTS technology to enable the design and construction of a demonstration plant achieving a TRL of 7 by the end of the project. The TRIFTS process has been thoroughly tested at the pilot scale (over the past two years) processing a 9-24 scfm slipstream of raw biogas into drop-in renewable transport fuel. The process is capable of utilizing both the carbon dioxide and methane portions of biogas and incorporates the biogenic carbon from them into the hydrocarbon backbone of the final fuel product of the process. In doing so the technology essential uses 100% of the biogas as a feedstock. The use of carbon dioxide (CO<sub>2</sub>) is a critical cost reduction step as it represents 40-50% of the total makeup of biogas effectively doubling the utilizable carbon compared to technologies that remove CO<sub>2</sub> utilizing expensive pretreatment processes. We have previously identified a candidate landfill with our project partners to implement 1,300 scfm biogas capacity plant and produce over 1,000,000 gal/yr of renewable cellulosic diesel. This renewable source of diesel resembles its petroleum counterpart both physically and chemically, passing ASTM D975 specifications, and can be used in current







Project Title: TRIFTS Biogas to Renewable Fuel Technology Evaluation
Project Applicant: Yolo County
Project Director/Principal Investigator: Ramin Yazdani
Project Investigators: Mr. Devin Walker (T2C-Energey), Dr. Troy Hawkins (Argonne National Lab), Professor Anthony Wexler (UC Davis-Air Quality Research Center)

The Yolo County Department of Community Services, Division of Integrated Waste Management is applying to evaluate the Tri-reforming and Fischer Tropsch Synthesis (trademarked TRIFTS<sup>®</sup>) Biogas to Renewable Fuel Technology. This project seeks to perform feasibility and technical demonstration testing to determine the best strategy to convert waste gas to energy at the Yolo County Central Landfill (YCCL). The main objective of this project is to

# **PROCESS ECONOMICS**

Scale (LFG Flowrate SCFM)	CAPEX	Annual OPEX	Annual Revenue	Annual Profit
500	\$3.5 MM	\$550 k	\$3.5 MM	\$2.1 MM
1000	\$5.2 MM	\$800 k	\$7 MM	\$4.5 MM
1500	\$6.7 MM	\$1 MM	\$10.5 MM	\$7.0 MM
2000	\$7.9 MM	\$1.2 MM	\$14 MM	\$9.5 MM
2500	\$9.1 MM	\$1.4 MM	\$17.5 MM	\$11 MM
3000	\$10.1 MM	\$1.6 MM	\$21 MM	\$14 MM
3500	\$11 MM	\$1.8 MM	\$24.5 MM	\$16.8 MM
4000	\$11.9 MM	\$2 MM	\$28 MM	\$19 MM

----- Interest Rate ----- Diesel Price ----- Raw Materials Cost Fixed Capital Investment \$8.0 \$6.0 \$4.0 \$2.0 -25% -15% -5% 35% 25% Net Present \$(2.0) \$(4.0) \$(6.0) \$(8.0) Parameter % Change

Sensitivity analysis results. Base case is based on 15% interest rate, \$3.24 per gal diesel price, \$2.09 per MMBtu for LFG cost and total FCI of \$8.5 million.

 Breakeven <u>No RIN credit</u> at 900 SCFM biogas production rate

#### **Assumptions**

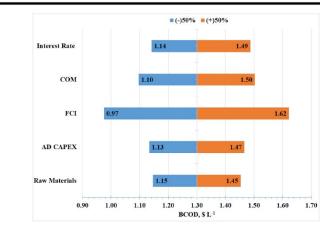
- 15% Interest Rate
- 35% Corporate Tax
- ➣ 5.5% FCI Maintenance Budget

- > 7 Full Time Staff
- Wholesale Pump Price = \$1.63
- RIN = \$4.47/gal diesel (D3 ~ \$2.63/RIN) EV=1.7

### **PROCESS ECONOMICS**

#### Effect of tipping fee on feedstock on BCOD and NPW.

Tipping Fee (\$ tonne <sup>-1</sup> )	Feedstock Cost (\$ tonne <sup>-1</sup> )	BCOD (\$ L <sup>-1</sup> )	NPW (Million \$)
0	55	1.57	-10.9
0 (base case)	28	1.30	0.00
0	0	1.02	10.9
28	0	0.80	19.7
55	0	0.58	28.6
83	0	0.36	37.4



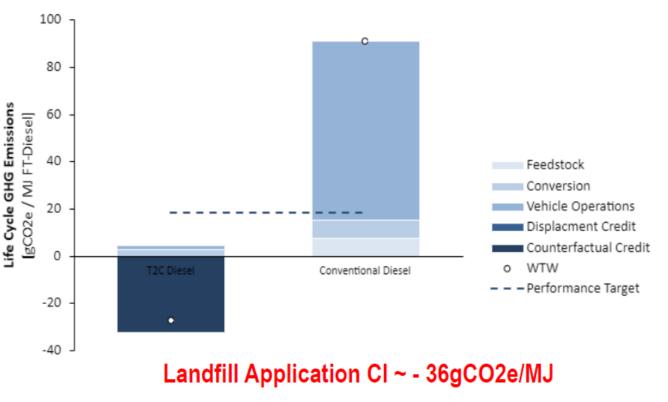
#### Economic comparison with published BTL modelling studies [72-74].

BTL Techno-economic Study	Interest on Capital Investment	Biomass Feed Capacity (dry tonne day <sup>-1</sup> )	Production Cost of Diesel ( $L^{-1}$ )
Gasification-FT synthesis [72]	10%	2,016	0.56
AD-BGTL	15%	186	1.20
Gasification-FT synthesis [73]	10%	1,920	0.73
Gasification-FT synthesis followed by hydroprocessing [74]	10%	2,000	1.19

#### This Includes AD (~doubles the CAP-EX)

# **ENVIRONMENTAL IMPACT**

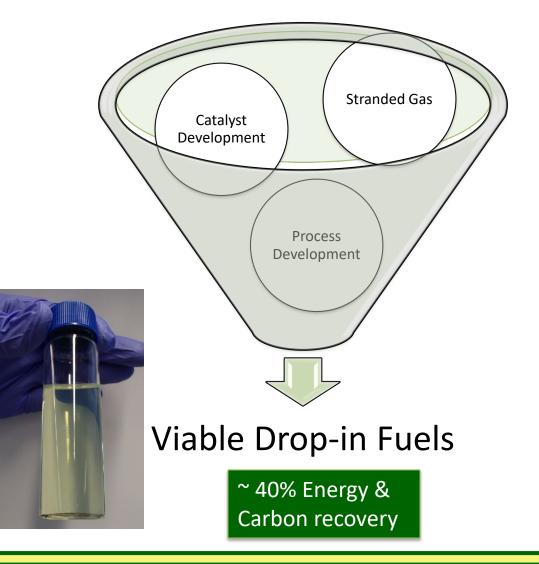
- HYSIS fully integrated with heat and mass recycle
- Biogas composition impacts (reactant feed auto tuning)
- ANL GREET model updated with TRIFTS Life Cycle Analysis
- Basic engineering design package (Global Docs completed)
  - Heat and mass balances
  - PFD's
  - General arrangement
  - P&ID's
  - Equipment / Instrument spec list
  - Control architecture
  - Pipe sizing and metallurgy study
- Engineering package Issued for Bids



#### **ANL GREET Model Carbon Intensity Score**

# **SUMMARY**

- Utilize most of Biogas Feedstock (CO<sub>2</sub> Utilization)
- Significant Reduction of Unit Operations
- Compatible with Current Infrastructure
- High Quality Value Added Product (Drop-In Diesel)
- Self Sufficient Process
- Produce D3/D7 RIN
- Vastly Improved Economics and Profitability, even in face of economies of scale



## THE TEAM







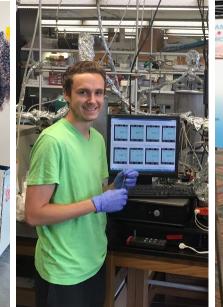














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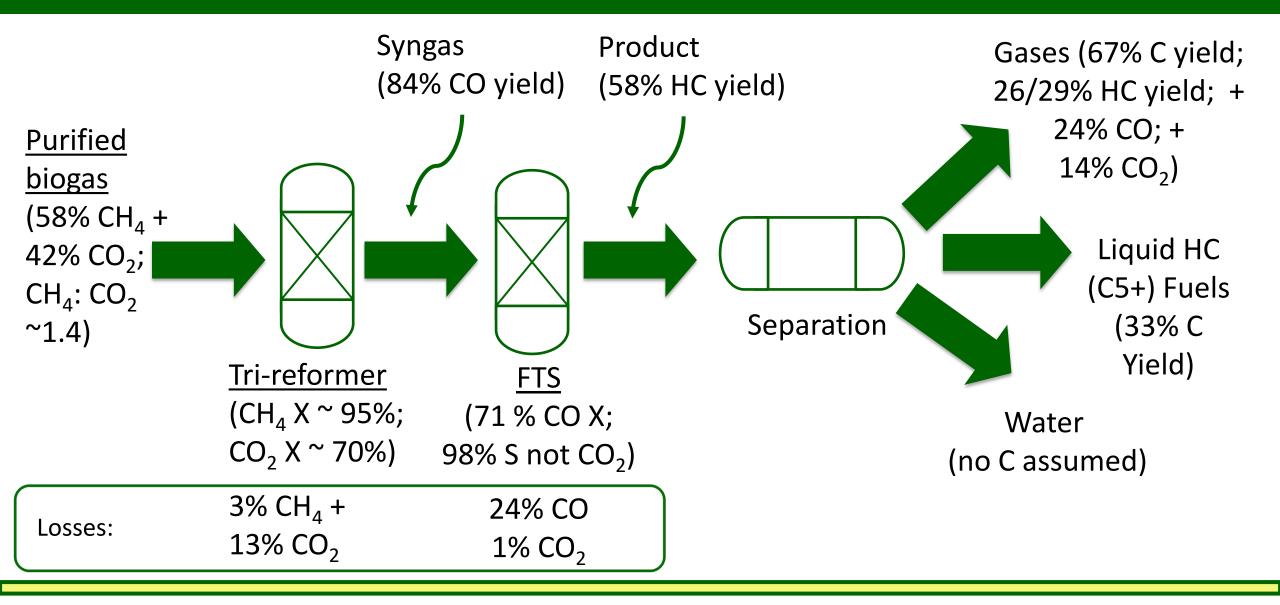




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### PARKED

# **TRIFTS PROCESS OVERVIEW\***



\* Neglecting purification train here (material losses minimal; energy losses vary)

# **OVERALL M&EBS**

