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Conversion of landfill gas to liquid fuels through TriFTS (Tri-reforming and Fischer-Tropsch Synthesis) process: A feasibility study

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ABSTRACT

Biogas produced in landfills contains large amounts of methane (a potent greenhouse gas) and hence requires collection and treatment according to EPA regulations. Tri-reforming of such biogas (CH_4+CO_2) is a combination of dry reforming, steam reforming, and partial oxidation to produce syngas (CO+H_2). This syngas can be converted to liquid hydrocarbons using Fischer-Tropsch Synthesis (FTS). A novel technology of combining tri-reforming and FTS (TriFTS) is proposed and utilized to convert landfill gas (LFG) to high value added liquid hydrocarbon fuels such as gasoline, diesel, and jet fuel. This article explores the feasibility of TriFTS from an experimental and process economics point of view.

Landfill gas collected from a local landfill was used in this study. After removing contaminant gases such as H_2S and NH_3 via condensation and adsorption, NiMg/$Ce_{0.6}Zr_{0.4}O_2$ pellets were used in a tri-reforming reactor to produce H_2 and CO in a ratio suitable for FTS. The conversions of CH_4 and CO_2 were 99% and 60%, respectively. The H_2/CO molar ratio was 1.7. In the FTS section, Co/SiO_2 eggshell catalysts were used to synthesize liquid hydrocarbon with high selectivity for middle distillate cuts. The CO conversion in FTS was 71% and the liquid hydrocarbon product was similar to that of low sulfur diesel.

The experimental results were used to conduct a preliminary economic analysis of a commercial scale TriFTS process. The results indicate that 45% of the energy contained in the LFG can be recovered in the liquid fuel generated, with the rest going to meet the energy demands of the conversion process including heat losses. The breakeven cost of diesel fuel produced was estimated at \$3.24/gal but reduces to \$2.71/gal if the LFG is assumed to be free of cost as would be the case for landfill operators. Additional renewable fuel credits will make the process even more economically attractive. This study suggests that conversion of LFG to liquid fuels is a promising new technology ripe for commercialization.

Keywords: landfill gas; tri-reforming; Fischer-Tropsch Synthesis; liquid fuel; waste-to-energy

Introduction

In 2010, the EPA estimated that 250 million tons of MSW were produced in the United States generating an estimated 215 billion cu.ft. of landfill gas (LFG) [1]. LFG contains a large fraction of methane. Methane, as a GHG, is 23 times more potent than carbon dioxide and landfills account for 17.1% of the human-made source of methane in the US. Methane emissions from landfills also represent a lost opportunity to capture and use a renewable energy resource [1]. EPA standards dealing specifically with methane emission includes Municipal Solid Waste Landfill New Source Performance Standards (NSPS) and National Emission Standard for Hazardous Air Pollutants (NESHAP) [1]. If the methane concentration at any location on the surface of a landfill exceeds 500 parts per million (ppm), the landfill must take action to reduce emissions [1]. According to the EPA [1], "*Of the 2,400 or so currently operating or recently closed MSW landfills in the United States, more than 550 have LFG utilization projects. EPA estimates that approximately 540 additional MSW landfills could turn their gas into energy*". Many landfills either flare the LFG to meet emission requirements (a waste of a valuable renewable energy source) or use engines that run using LFG to generate electricity which is then sold to the electric utility. The electric utilities generally pay only what it costs them to produce electricity. Thus, the revenue from power production is often not sufficient to meet the costs of running an LFG-power plant.

LFG may also represent a zero cost feedstock that can be converted into highly desired renewable liquid fuels that are in demand both in-house (diesel for landfill trucks) and outside markets (transportation sector). The garbage-trucking sector in the US consumes nearly one billion gallons of diesel fuel annually with the average garbage truck using 6000 gal/year, making up 1.1% of the total US diesel consumption [2]. This equates to a $3-4 billion dollar expenditure on diesel fuel in this sector alone. Current waste-to-energy technologies, such as power generation or Compressed Natural Gas (CNG) production from LFG, are inhibited by high capital costs and low economic recovery [3]. Current technologies also have stringent input and output specifications in order to function as designed. If feedstock is outside the required specifications, LFG is flared, and the energy resource is wasted. The agriculture and waste industries combined use 4.2 billion gal/yr of diesel, representing over a $10 billion expenditure each year.

TriFTS (Tri-reforming and Fisher-Tropsch Synthesis) is a proposed new technology (Fig. 1) to first convert LFG to syngas and then produce liquid hydrocarbon fuels using Fischer-Tropsch Synthesis (FTS). This technology produces a renewable liquid fuel while satisfying EPA regulations for reducing LFG emissions at municipal solid waste (MSW) facilities. Using the green-fuel produced to power the landfill trucking fleet reduces greenhouse gas emissions not only from the landfill site but from the vehicles as well. Because the feedstock for the TriFTS process must be collected in existing landfills, there is no added cost for the feedstock and a closed loop process is created from feedstock to end user.

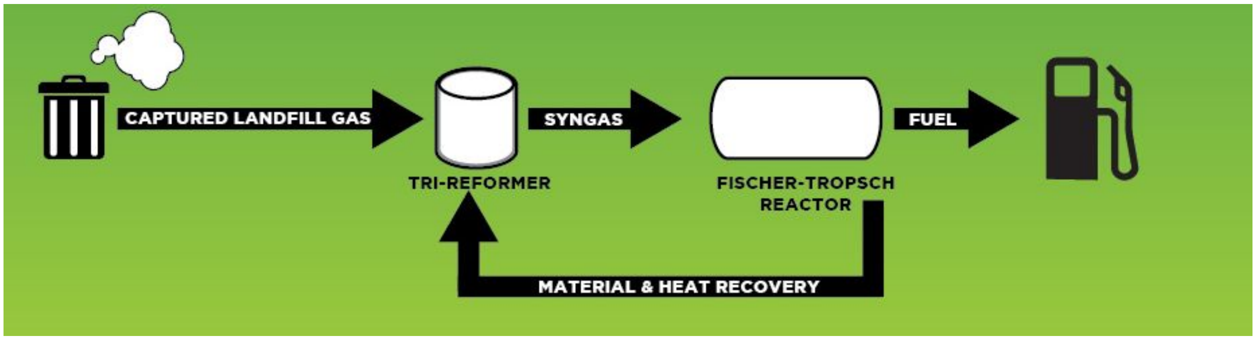

Fig. 1 Overview of TriFTS process for converting LFG to liquid fuels.

LFG is composed primarily of a mixture of CH_4 and CO_2 with some contaminants such as H_2S, NH_3, H_2O, non-methane organic compounds, air, and siloxanes (Table 1). Currently, the

EPA regulates these emissions by requiring landfill operators to install sensors (to monitor the environmentally harmful components) and collection systems to capture the gases to mitigate CH_4 emissions [1]. Landfill operators currently have three choices currently: burn off the methane in a flare, use the low energy gas to produce power and sell to the grid, or purify the LFG to produce CNG. The economics of such conversion processes is diminished by the decreasing price of natural gas due to discovery of fracking that extracts more natural gas from underground reservoirs. The key differentiator of the proposed technology is the high value added nature of the product and the recovery of carbon contained in the CO_2.

Table 1 Typical Landfill Gas Composition [1].

Constituent Gas	Concentration in LFG	
	Range	Average
Methane	35-60 %	50 %
Carbon Dioxide	35-55 %	45 %
Nitrogen	0 -20 %	5 %
Oxygen	0-2.5 %	<1 %
Hydrogen Sulfide	1-1,700 ppmv	21 ppmv
Halides	NA	132 ppmv
Water Vapor	1-10 %	NA
Nonmethane Organic Compound (NMOC)	237 to 14,294 ppmv	2,700 ppmv

The simplest and cheapest method for processing LFG is to burn it using gas flares [4]. However, these flare type technologies produce environmentally harmful compounds such as carbon monoxide, NO_x, SO_x, dioxins, and heavy metals with no capture of the energy released. A technology sold to the landfills is to collect, clean, and burn the LFG to run generators to produce electricity sold to the grid. Electricity produced by the combustion process show low efficiencies ranging from 30-35% [5]. These low efficiencies are due to the energy consumption for pre-processing of the LFG before it is sent to the generators and the inefficiencies inherent in the turbines and generators themselves. The cleanup process involves removal of water, sulfur, and siloxane compounds and condensing of heavier molecular weight compounds. This cleanup step is critical to this process in order to avoid contamination and corrosion of the pipeline and generators. Many states require investor-owned utilities to pay independent power producers, such as landfills, only what it would cost the utility company to produce the electricity themselves by the cheapest means possible. This lowers the financial incentives for implementing power recovery systems from landfills unless favorable tariffs for the generated electricity can be negotiated with the local utility provider.

Another development in the LFG processing industry is the separation, collection, cleaning to produce compressed natural gas (CNG). It is expensive to process LFG to pipeline quality due to the cost of separating CO_2 and N_2, dewatering, desulfurization, and other cleaning steps involved. Another barrier to this technology is that the existing infrastructure for CNG distribution for use in transportation vehicles is currently limited in size and scope. Expensive fueling stations and engine modifications must be in place to use this fuel effectively (only 10% of all waste trucks are capable of using LNG). Retrofitting trucks for this technology is in excess of $40,000 per vehicle.

An advantage of the proposed TriFTS process is the premium price of liquid fuel compared to the price of natural gas and electricity when compared on a per Btu basis. As a result, waste management companies would be able to solve an environmental problem while simultaneously producing renewable liquid fuels. Carbon credits and government subsidies for renewable liquid fuels will be an added bonus.

The objective of this work is to investigate the feasibility and techno-economics of combining tri-reforming and FTS (TriFTS) to convert real landfill gas to liquid hydrocarbon fuels. LFG collected from a nearby landfill was used for these bench-scale experiments. The landfill gas was pretreated to remove impurities prior to introduction to a tri-reformer and the syngas produced was fed to an FTS reactor. The yield and conversion data from the bench-scale unit was used for conducting a preliminary economic analysis of a commercial scale process for converting LFG to liquid fuels. The sensitivity of the process economics to potential variations in market conditions and processing performance is examined.

TriFTS process description

The TriFTS process (Fig. 2) consists of the following sections: Pretreatment of the LFG to remove contaminants, tri-reformer to produce syngas followed by FTS reaction to produce a mixture of hydrocarbons, water and light gases. The products from the FTS reactor is send to a separations section where the product fuel is recovered. Each section is now further described.

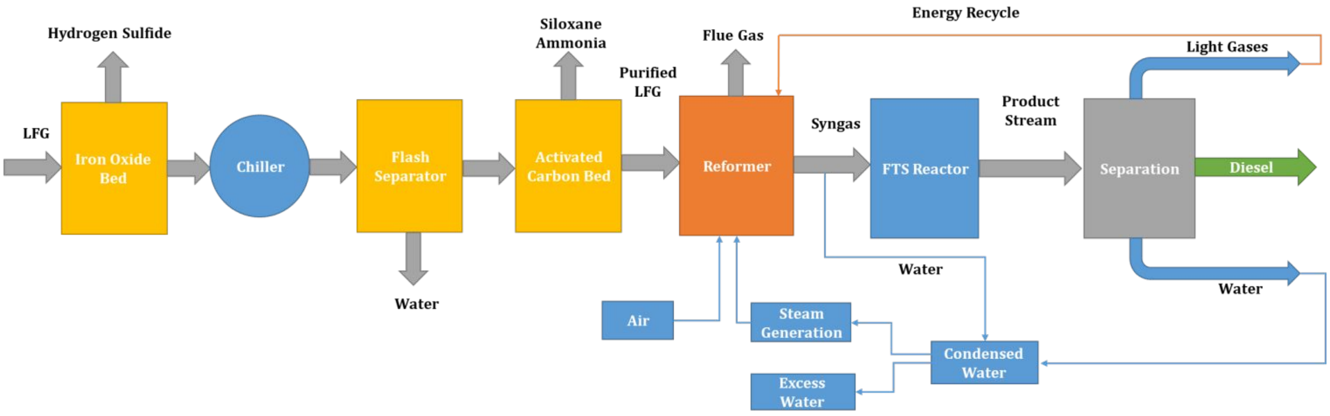

Fig. 2 Block flow diagram of the TriFTS process.

Contaminant removal

As shown in Table 1, LFG can contain significant amounts of contaminants the major ones being H_2S, NH_3, water, and siloxanes. The sulfur and siloxanes[6] poison the catalysts used in later steps and therefore must be removed. Various technologies have been proposed and are recently summarized i [7]. Based on that study, the purification step was designed as follows[8].: an iron-oxide bed to remove the hydrogen sulfide, a chiller to cool and condense the water and an activated carbon bed to remove the remaining organic contaminants including NH_3 and siloxanes. The purified gas is then sent to the tri-reformer.

Tri-reforming

Tri-reforming [9-13] refers to simultaneous reforming of methane using oxidative CO_2, steam, and O_2. It is a synergetic combination of endothermic CO_2 and steam reforming, and exothermic oxidation of methane.

$$\text{Dry Reforming:} \quad CH_4 + CO_2 \longrightarrow 2\,CO + 2H_2 \quad (1) \quad \Delta H = 247.3 \text{ kJ/mol}$$

$$\text{Steam Reforming:} \quad CH_4 + H_2O \longrightarrow CO + 3H_2 \quad (2) \quad \Delta H = 206.3 \text{ kJ/mol}$$

$$\text{Partial Oxidation:} \quad CH_4 + 1/2O_2 \longrightarrow CO + 2H_2 \quad (3) \quad \Delta H = -35.6 \text{ kJ/mol}$$

The tri-reform process eliminates the serious problem of carbon formation and high energy consumption commonly seen in CO_2 reforming by incorporating H_2O and O_2. Heat is generated in-situ that can be used to increase energy efficiency and achieve a thermo neutral balance of reactions [14, 15]. H_2 and CO selectivity can also be adjusted by controlling the amount of steam and CO_2 added to the reaction [16-22]. Song and Pan [21] compared tri-reforming to dry and steam reforming and determined that it consumes less energy while producing less CO_2 per unit of desired syngas (H_2:CO = 2). Tri-reforming, respectively, uses 45.8% and 19.7% less energy and produces 92.8% and 67.5% less CO_2 compared to dry and stream reforming [21].

Tri-reforming catalyst must be thermally stable, have a high surface area, provide resistance to coke formation, and be economically advantageous in order to be feasible. Metals that have shown to have a good activity and selectivity for reforming reactions include Ni, Pt, Rh, and Ru [23]. Ni based catalysts show good potential for reforming methane providing a more economically friendly option over noble metals and thus most research has focused on developing novel Ni catalyst formulations. However, nickel has the disadvantage of being susceptible to coke formation [15, 23]. In this work, a Ni-MgO-(Ce,Zr)O_2 tri-reforming catalyst d [9] was selected. This unique combination of catalyst metal and oxide metal support with appropriate metal loadings can be used to convert a mixture of CH_4, CO_2 and O_2 to syngas with H_2:CO ratio in the range of 1.7-2.2 that is highly suited for converting it to liquid hydrocarbon fuels. The high temperature (~ 800 – 1000 °C) necessary for the tri-reforming process can lead to the deactivation of catalysts, indicating the catalysts should be thermally stable [24].

Fischer Tropsch Synthesis

FTS is a well-researched process playing a major role in Gas-to-Liquid (GTL) technology used to convert natural gas to liquid hydrocarbons [25-29]. The synthesis of hydrocarbon liquids and waxes using coal derived syngas on Co and Fe catalyst by Franz Fischer and Hans Tropsch lead to the naming of this synthesis technique [30]. The main reactions involved are:

$$(2n+1)\ H_2 + n\ CO \longrightarrow C_nH_{2n+2} + n\ H_2O \qquad (4)\ \Delta H = \sim\!-150\ \text{kJ/mol}$$

Here n can range from 1(methane) to as high as ~30 (waxes). In addition smaller quantities of alcohols and olefins may also be produced. FTS is a polymerization process in which hydrocarbons are added stepwise to a growing aliphatic chain on the catalyst surface. Related research during the last 10 years has led to the development of a cobalt catalyst with an eggshell morphology[31, 32]. This research showed that it is possible to tailor the FTS catalyst to produce a highly selective product distribution, especially concentrated around the middle distillate region.

Product separation

The main products from the FTS reactor can be easily separated into 3 parts: The liquid hydrocarbons consisting of C5+, light gases consisting of unconverted CO, H_2 and C1-C4 gases. Cooled product stream from the FTS reactor is sent to a 3-phase separator to remove the water and light gases. The liquid hydrocarbon may require further processing depending on its composition.

Methodology

The analysis was carried out as follows. First the integrated process was evaluated using a bench scale unit using LFG collected from a local landfill. The data from the bench scale run was then used to carry out a preliminary design and economic evaluation of a commercial scale TriFTS process using Aspen Plus simulator. Details of each step are given below.

LFG collection and purification

The LFG was collected from Sarasota County Solid Waste Facility. During the collection of the LFG, the main LFG header pressure was measured at only 1.6 psig, which had to be compressed into cylinders up to 2265 psig. A compressed natural gas (CNG) refueling unit from BRC FuelMaker (Model FMQ 2 P36) capable of compressing natural gas at 0.4 psig up to 3600 psig at a flow rate of 1.3 scfm was used. Two 1-liter volume filter beds of Du-Cal DRIERITE (8 mesh) were used in a parallel configuration to ensure that the inlet LFG fed to the compressor was completely dry. This would avoid any moisture accumulation and possible corrosion in the pressurized cylinders. A Pietro Fiorentini gas governor was placed prior to the compressor inlet to regulate pressure to 0.4 psig (recommended pressure supply to compressor). Stainless steel ¼ inch tubing was connected to the outlet of the compressor and a check valve was installed as a safety precaution. The tubing was coiled and submersed in an ice water bath to regulate compressed gas temperature below 37 °C and connected to a gas cylinder. The total volume of LFG collected and transported to the laboratory using a truck was 565 standard ft^3. The gases (air, landfill gas, CO and H_2) were analyzed using a gas chromatography-mass spectrometer (GC-MS, GC: 6890N, MS: 5975C, Agilent Technologies) with N_2 as an internal standard gas.

Filter beds were composed of Sulfatreat 410CHP, silica gel (Super Adsorbent Siloxane Silica Gel, granular, 6 × 12 mesh), and BPL activated carbon (AC, Calgon) that were used to remove the sulfur, siloxane, and halide compounds, respectively. The LFG first went through the Sulfatreat filter bed. After the Sulfatreat filter bed, a cooling unit capable of lowering the LFG to approximately 5 °C followed by a knock out pot to remove condensed water. The silica gel bed was located after the condensed water knock out pot. The AC bed was the final filter bed to purify LFG. Cost estimates for LFG purification was evaluated based on a recent study done by Elwell et al. [8].

Catalyst preparation

$NiMg/Ce_{0.6}Zr_{0.4}O_2$ pellets were used for the tri-reforming section. $Ni(NO_3)_2{\cdot}6H_2O$ (99.9985% pure; Alfa Aesar), $Mg(NO_3)_2{\cdot}6H_2O$ (99.97% pure; Alfa Aesar), $Ce(NO_3)_3{\cdot}6H_2O$ (99.5% pure; Alfa Aesar), $ZrO(NO_3)_2{\cdot}xH_2O$ (99.9% pure; Alfa Aesar), deionized (DI) water, and NH_4OH (NH_3 assay: 28-30%; VWR International, LLC) were used to synthesize $NiMg/Ce_{0.6}Zr_{0.4}O_2$ pellets. Details on the preparation of the $NiMg/Ce_{0.6}Zr_{0.4}O_2$ pellets are described in a prior related publication [33].

For the FTS process, eggshell Co catalysts supported on SiO_2 spheres were prepared through precipitation of cobalt nitrate solution. The catalyst was prepared using a procedure describe in a related prior publication [31]. Spherical silica gel (CARIACT-Q10) were soaked in heptane for 24 h in a glove box. Cobalt nitrate hexahydrate was dehydrated at around 75 °C for approximately 2 h. The dehydrated cobalt nitrate was dissolved in ethanol, and 2% of DI water in volume was added. The soaked spheres were dried at ramp rate of 1 °C/min up to 60 °C. The cobalt nitrate ethanol solution was heated to 70 °C and the hot cobalt nitrate solution was added onto the partially dried SiO_2 spheres. The urea/ethanol solution (10 g urea added in 100 mL ethanol) was added dropwise to hot bath of cobalt nitrate and SiO_2 spheres while continuously stirring until gradual rise of pH to 3.5 - 3.8. The spheres were immediately removed from the nitrate urea solution and then rapidly dried in a vacuum furnace at 100 °C for 24 h. Finally, the spheres were calcined in hydrogen at 400 °C with a ramp rate of 2 °C/min for ~ 1 h.

Bench-scale TriFTS process

A bench-scale version of the TriFTS process was set up (Fig. 3 and Table 2) in order to evaluate the performance of each of the processing steps.

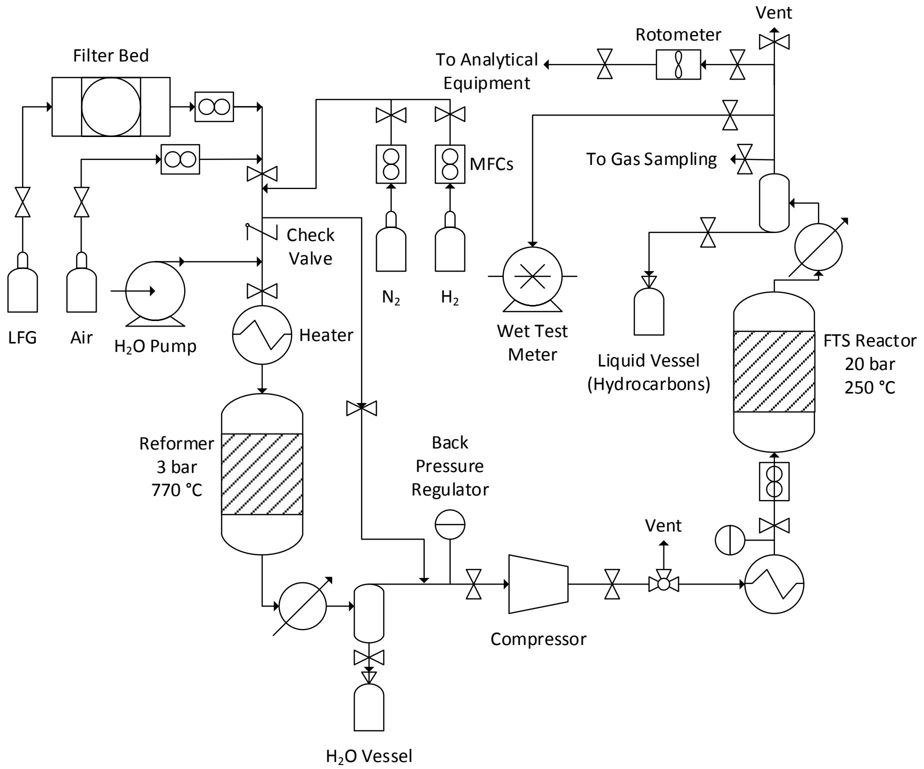

Fig. 3 A simplified schematic diagram for the TriFTS integrated system to convert LFG to liquid fuel.

Table 2 The conditions of the TriFTS run.

Characteristics	Value
Molar ratio of LFG/air/steam	1: 0.56: 0.36
Tri-reforming temperature (°C)	770

Tri-reforming pressure (bar)	3
Tri-reforming GHSV (h^{-1})	11,600
FTS temperature (°C)	250
FTS pressure (bar)	20
FTS GHSV (h^{-1})	2,800
Condition for separating liquid and gas	Condenser: ~ 0 °C

Mass flow controllers (MFC) from Alicat Scientific, Inc. (Tucson, AZ, USA) and Brooks Instrument (Hatfield, PA, USA) were used to adjust the gas flow rates. The gases include landfill gas, air (dry grade, Airgas, Inc.), H_2 (ultra-high purity, Airgas, Inc.) and N_2 (ultra-high purity, Airgas, Inc.). The molar ratio of LFG/air/steam was 1: 0.56: 0.36. All oxygen was consumed during the tri-reforming reaction. The steam was provided using a LC-10 AS pump to deliver water into the heated feed gases.

The tri-reforming test was run at 3 bar (standard deviation: 0.14 bar) in a fixed-bed reactor with 5.05 g of NiMg/$Ce_{0.6}Zr_{0.4}O_2$ pellet catalysts at 770 °C (standard deviation: 2.4 °C). The gases including purified LFG, air, and steam were heated using a tube furnace (Lindberg/Blue, temperature range: 100 – 1100 °C). The temperature at the inlet to reformer was approximately 120 °C. SiC was used to hold the catalyst bed, where a thermocouple was inserted, and also to enhance heat transfer and keep the bed at a uniform temperature. The GHSV was 11,600 h^{-1}. The reactor tube (seamless nickel alloy pipe 625) has an inside diameter of 16 mm. The reforming catalysts were reduced at 860 °C for 2.8 h in a 43% H_2/N_2 (N_2 = 200 sccm; H_2 = 150 sccm) prior to the reaction. The time-on-stream for reaching steady-state was ~ 4 h. The mass balances of carbon or hydrogen were determined using the total moles of carbon or hydrogen out as products divided by the total moles of carbon or hydrogen in as reactants. The overall error in the carbon and hydrogen mass balance was determined as 3% and 1%, respectively.,

The gas exiting the reformer was cooled and compressed to 20 bar pressure. No additional H_2 or CO was injected. The temperature at the inlet to FTS reactor was approximately 250 °C. The FTS test was run at 20 bar in a fixed-bed reactor with 3.10 g of Co/SiO_2 eggshell sphere catalysts at 250 °C (standard deviation: 3.3 °C). The FTS catalyst (Co/SiO_2 spheres) was reduced at 400 °C for about 14 h in a 50% H_2/N_2 (N_2 = 200 sccm; H_2 = 200 sccm) at 1 bar prior to the reaction. The GHSV in the FTS section was 2,800 h^{-1}. The total running time for the whole TriFTS process was around 57 h.

Methodology for preliminary design and economic analysis

The results from the bench scale experiments were used as a basis for the preliminary design and economic evaluation of a commercial scale TriFTS process (Fig. 2) in order to estimate the cost of manufacturing and sensitivity to parameters. A basis of 2500 SCFM of LFG typical of large landfills was used for this analysis.

Aspen Plus V9 was used to model the process. Aspen Plus is a simulation tool that helps predicting the behavior of a chemical process through mass balance, energy balance, fundamental thermodynamic relationships, and reaction kinetics. The purification steps were modeled using simple separation blocks. The tri-reformer and FTS reactors were modeled using RYIELD (a yield based reactor model) using the yield data obtained from the bench-scale runs.

The process involves intensive heating and cooling; consequently, heat integration is incorporated where possible minimize heat requirements for the process. Heat integration is done through a serious of heat exchangers to simultaneously cool down product streams while providing heat to feed streams. For exothermic unit operations like the FTS reactor, boiler feed water was used to recover the heat while maintaining the reactor temperature constant. Additional cooling for the process is achieved via cooling water and chilled water to facilitate the separation processes. Phase specific heat transfer coefficient values are used to predict the required heat transfer areas required for each heat exchanger.

In addition to heat recovered from heat exchange, the tri-reformer requires additional energy to reach the desired reformer temperature and for the endothermic heat of reaction. This heat is provided by recycling 63% of the produced fuel gas which is estimated based on 80% combustion efficiency.

The sizing of each equipment was based on the Aspen Plus simulation results. Costing method provided by Turton et al [34] was followed to estimate the bare module cost for each piece of equipment.. Some parts are costed differently due to their configurational complexity such as the reformer which consists of a furnace and tubes. The furnace was costed as carbon steel reformer furnace while reformer tubes costed as seamless nickel alloy 625 due to the high temperature durability and the exceptional fatigue strength. The reformer furnace thermal efficiency is assumed to be 80%.

The most recent chemical engineering plant cost index (CEPCI) for 2017 is found to be 561.2 which is used to adjust the equipment costs given in Turton et al. [34, 35]. Economic analysis was based on 350 days of operation. All cost figures are given in 2017 US dollars. A salvage at the end of the plant life is assumed to be 10% of the fixed capital investment (FCI). The plant life is assumed to be 15 years with a construction period of 2 years. 60% of the Fixed Capital expenditure is assumed for the first year of construction, and 40% during the second year construction. The land cost that is assumed to be 2% of the fixed capital investment is assumed to take place prior to construction. In addition, the working capital which is assumed as 15% of the fixed capital investment takes place at the end of construction to account for plant startup and finance the first few month of operation. Modified accelerated cost recovery system (MACRS is used to compute tax burdens). This allows for the highest cash flow during the early years.

Results and discussion

Pretreatment of landfill gas

The composition of LFG (collected at Sarasota Landfill) is shown in Table 3. Sulfur composition was measured using Drager tubes (Draeger 8101831) capable of measuring hydrogen sulfide in the 1-200 ppm range. Halide composition was measured using Drager tubes (Draeger 6728411) capable of measuring chlorinated halides in the range of 0.3-5 ppm. Siloxanes were measured as octamethylcyclotetrasiloxane (D4) per GC-MS.

Table 3 Composition of LFG used in this study and comparison with literature.

	This study	Reference [36]
Compound	Mole percent (%)	Volume percent (%)
CH_4	56.7	45 – 57
CO_2	40.5	37 – 41
N_2	2.4	1 – 17
O_2	0.4	0 – 2

H_2S_2 (ppm)	68	
H_2S		< 1
CO (ppm)	6	
Siloxanes (ppm)	4	
Halides (ppm)	3	
H_2O		4 – 7
Organic aromatics		trace

The same contaminant analysis was also done to samples taken directly after the purification bed filters throughout the LFG experimental runs except that the sulfur was measured by Drager tubes (Draeger 8101991) capable of measuring Hydrogen Sulfide in the 0.2-6 ppm range. After the LFG cleanup, the outlet gas did not contain sulfur, siloxane, and halide compounds.

Results of bench scale experimental TriFTS runs

In the tri-reforming section, the CH_4 conversion, CO_2 conversion, and H_2/CO molar ratio were 99% (standard deviation: 0.2%), 60% (standard deviation: 1.4%), and 1.72 (standard deviation: 0.03), respectively. Similar results were obtained in previous research using this catalyst for tri-reforming of surrogate biogas [33], as well as other researchers at similar conditions. Dwivedi et al. determined CH_4 and CO_2 conversions of 98% and 19%, respectively, during tri-reforming of methane (CH_4 to steam molar ratio was 1: 0.88) at 3 bar and 850 °C.[37]. Chein et al. reported CH_4 conversion and H_2/CO molar ratio of ~ 99% and 1.4, respectively, during tri-reforming of methane at 10 bar and 800 °C[38].

The coke formation rate was 2.1 × 10^{-4} mol/(g_{cat}*h), indicating the high coke resistance of the catalysts [9, 33]. In addition, NiMg/$Ce_{0.6}Zr_{0.4}O_2$ catalysts were shown to be thermally stable and resistant to coke deposition during the tri-reforming of surrogate biogas. At 882 °C and 3 bar, the CH_4 conversion and CO_2 conversion were around 95% and 39%, respectively [33].

During the FTS section, the CO conversion, gas yield, liquid yield, water yield, and liquid fuel yield were 71%, 71 wt%, 29 wt%, 18 wt%, and 11 wt%, respectively (shown in Table 4). Water, light hydrocarbons (< C6) and CO_2 were the byproducts. The coke formation rate of Co/SiO_2 catalysts was approximately 4.4 × 10^{-5} mol/(g_{cat}*h), suggesting the catalysts were highly resistant to the coke deposition. For comparison, Otter et al. studied FTS using Co/SiO_2 catalysts and obtained a CO conversion of 35% at 20 bar, 220 °C and H_2/CO molar ratio of 2.0 [39]. Li et al. studied the FTS using the Co/SiO_2 catalysts and obtained the CO conversion of 27% at 20 bar, 210 °C and H_2/CO molar ratio of 2.0 [40]. Oh et al. studied FTS using Co/SiO_2 catalysts and obtained the CO conversion of 69% at 20 bar, 240 °C, 2,000 L/kg_{cat}/h, and H_2/CO molar ratio of 2.0 [41]. Prieto et al. studied the FTS using the Co/SiO_2 catalysts and obtained the CO conversion of 14% at 20 bar, 220 °C, and H_2/CO molar ratio of 2.0 [42].

Table 4 The results of the TriFTS run.

Characteristics	Value
Liquid fuel production rate (g/h)	1.3
Water production rate (g/h)	2.2

Gas production rate	8.4
Liquid fuel product composition, weight %	$C_4 – C_{12}$ hydrocarbons: 54.4 $C_{13} – C_{25}$ hydrocarbons: 45.0 C_{25+} hydrocarbons: 0.6
Gas product composition (mol %)	CO_2: 14.9 H_2: 9.10 CO: 18.6 N_2: 38.4 CH_4: 17.5 C_2H6: 0.79 C_3H_8: 0.33 C_4H_{10}: 0.19 C_5H_{12}: 0.15
CH_4 selectivity in FTS section (mole %)	~ 38
CO conversion (%)	71
Gas yield (wt.%)	71
Liquid yield (wt.%)	29
Water yield (wt.%)	18
Liquid fuel yield (wt.%)	11

The liquid fuel properties is compared with the No. 2 Diesel Specification and commercial diesel in Table 5. The liquid fuel has a lower specific gravity and higher net heat value than commercial diesel. In addition, the liquid fuel has the same cloud point and pour point to those of commercial diesel. The liquid fuel has a higher cetane index than No. 2 Diesel Specification. By distilling the lighter hydrocarbons out, the liquid fuel could easily meet ASTM D93 for flash point. In addition, the liquid fuel distilled at 55 °C passed all No. 2 Diesel fuel specifications. These results show that the liquid fuel produced utilizing actual LFG through TriFTS will be an excellent candidate as a drop-in fuel that could be utilized by today's diesel engines with no modifications to the engine needed. In fact, the high cetane index of the liquid fuel will contribute to less knocking within the diesel engine and therefore have a smoother combustion cycle compared to commercial diesel leading to extended engine lifetimes and therefore lower operational cost to run the engine.

Table 5 The properties of liquid fuel produced from TriFTS, No. 2 Diesel Specification and commercial diesel.

Characteristics	Liquid fuel	Liquid fuel after distillation	No. 2 Diesel Specification	Commercial diesel, tested in our lab
Specific gravity (g/mL, ASTM D4052)	0.739	0.749	-	0.822
Cetane index (ASTM D976)	84.5	72.7	≥ 40	57.6
Cetane index (ASTM D4737)	92.3	83.4	≥ 40	59.7
Flash point (°C, ASTM D93)	49	57	≥ 52	87
Cloud point (°C, ASTM D2500)	-6	-3	-	-6
Pour point (°C, ASTM D97)	-9	-6	-	-9
Net heat value (MJ/kg, ASTM D3338)	44.52	44.36	-	43.16

Results of economic analysis of the TriFTS process

A summary of mass and energy balances based on the results of Aspen Plus simulation is presented in Fig. 4. This shows that 45% of the energy contained in the feed LFG is recovered in the diesel product. Further 55.4 gal of diesel is produced per ton of LFG fed to the process (at the specified rate of 2500 scfm, there is 123 tons/day of LFG fed to the process and produces 6800 gal/day of diesel fuel). Water is a major byproduct of the reaction and must be treated as it contains some dissolved organics. A significant portion of the water produced in FTS reactor is recycled back to the reformer.

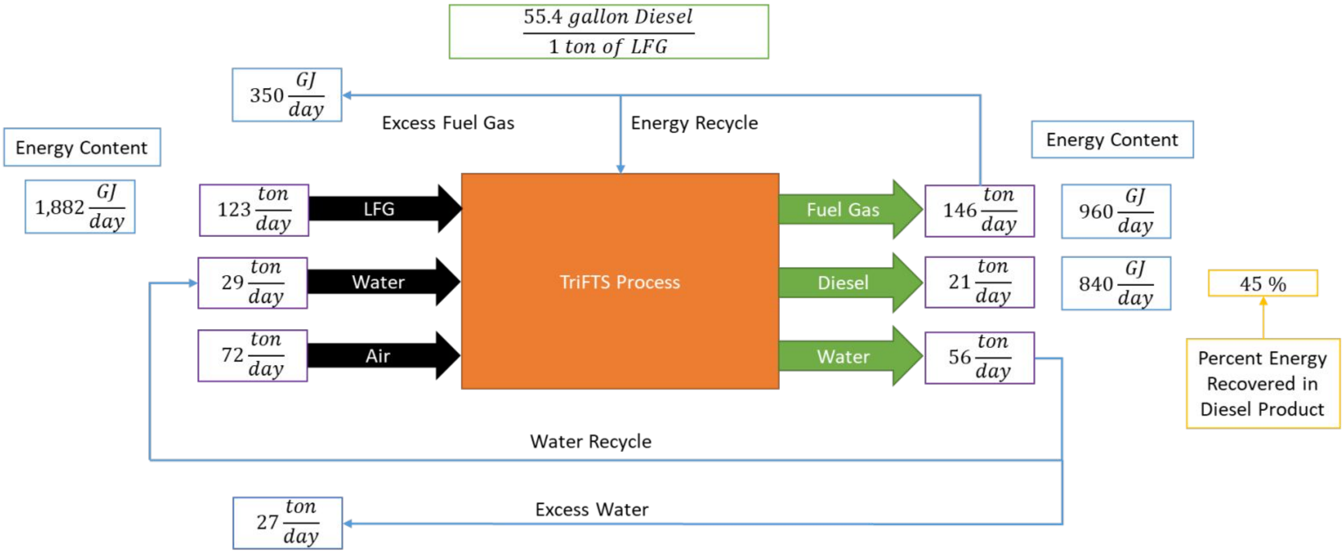

Fig. 4 Overall mass balance and energy recovery. Basis: 2500 scfm of LFG. The diesel yield is about 6,800 gal/day.

Capital costs

The total capital cost for the process was estimated at $8.5 million. The main units include compressors, heat exchangers, reactors, etc. The results indicate that compressors, reformer and FTS reactors, and heat exchangers play a significant role in the equipment cost (Fig. 5).

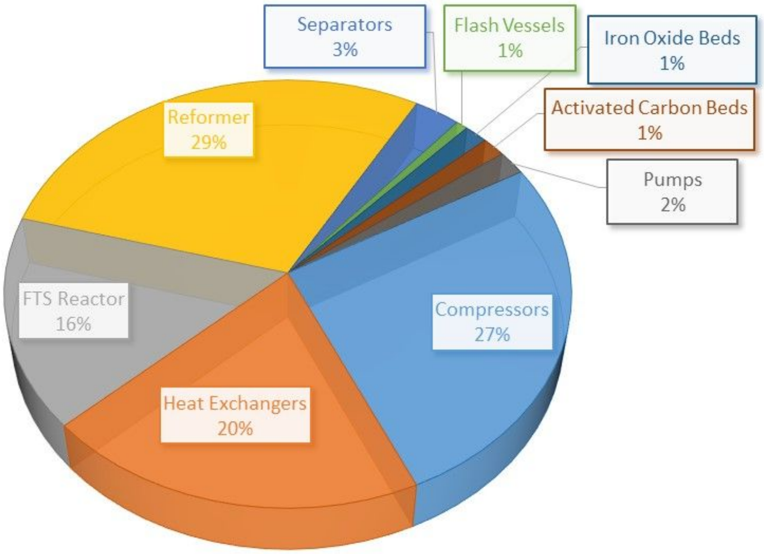

Fig. 5 Fixed capital costs breakdown. Costs are percent of \$8.53 million total FCI.

Manufacturing costs

The cost of operating labor is estimated based on the most recent annual wage data for chemical plant operators which is estimated to be \$60,800 per year [43]. Number of operators per shifts is based on 2 main operational sections: the tri-reforming unit and FTS reactor unit.

Raw material cost is mainly attributed to cost of the landfill gas, media needed for LFG purification, and catalyst needed for the reformer and FTS reactor (Table 6). LFG is assumed to cost \$2.09/MMBTU (70% of the average price of natural gas in 2017[44]). Iron sponge cost about \$ 0.35-1.55 per kg H2S removed [45]. A cost of \$1.55/kg H2S removed to is used to estimate the cost iron sponge media needed. The cost of activated carbon media is \$1.20 per pound which leads to annual cost of about \$18,800 per year for two beds based on the breakthrough time [8]. Cost of the tri-reformer and FTS reactor catalyst are based on nickel oxide and cobalt/silica, respectively[46-48].

Table 6 Annual raw materials cost (Thousand $/yr).

Iron Sponge	163
Activated Carbon	19
LFG	1,458
Nickel Oxide Catalyst	63
Cobalt Silica Catalyst	39
Total cost of raw materials	1,742

Waste treatment for the disposal of the spent packing material is estimated to be $36 per ton [49], while cost of wastewater treatment is $56/1000 m^3 [34]. Utilities to operate the plant include electricity, process water, cooling water, and chilled water. Cooling water (at 30 ^oC) and chilled water (at 5 ^oC) are used to cool down process stream to promote proper separation and contaminant removal. Cooling and chilled water costs are estimated to be $14.8/1000m^3 and $185/1000m^3, respectively [34]. Electricity cost is estimated at 6.79 cents per kWh [50]. Cost of process water is estimated to be $0.067/1000 kg [34]. The waste fuel gas was assumed to be converted to electricity at 20% efficiency to recover 810 kW of energy thus lowering the cost of electric utilities.

Fig. 6 shows the distribution of the cost of operating labor, raw material, utility, and waste treatment. The total utility cost was estimated at $434,000 made up of $23,000 for cooling water, $46,000 for chilled water, and $365,000 for electricity.

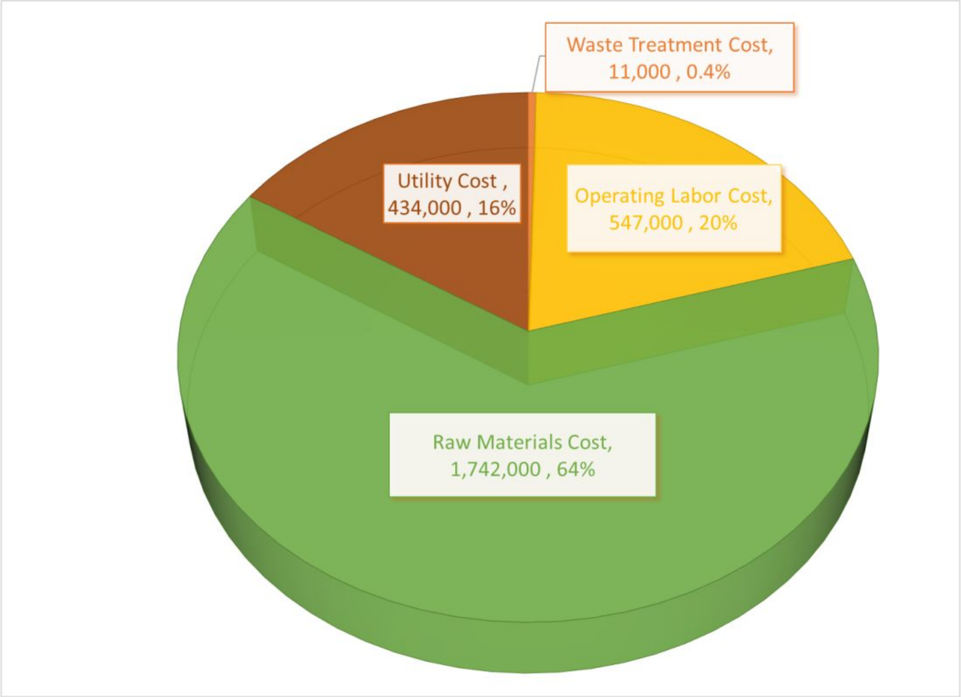

Fig. 6 Manufacturing cost breakdown. Total direct manufacturing cost is estimated at $5.72 million.

Breakeven cost of diesel

The breakeven cost of diesel (BCOD) is calculated based on 20% taxation rate and MACRS depreciation for 5 years with an interest rate of 15% on the total capital investment. Breakeven price of diesel is calculated to be $3.24/gallon which is defined as the price at which the NPW is equal to zero at the end of plant life, i.e. year 15. If landfill gas is free of cost, the BCOD $2.71/gallon, which is comparable with 2017 average diesel prices in the U.S [51].

Sensitivity analysis

Since diesel price is subject to change on regular basis, a sensitivity analysis was constructed to study the effect of diesel price fluctuations on the NPW. Moreover, other key parameters such as interest rate, raw materials cost, and fixed capital investment which could potentially affect the profitability of the plant were added to the sensitivity study. Fig. 7 shows the results of the sensitivity analysis study. The process profitability is most sensitive to diesel price.

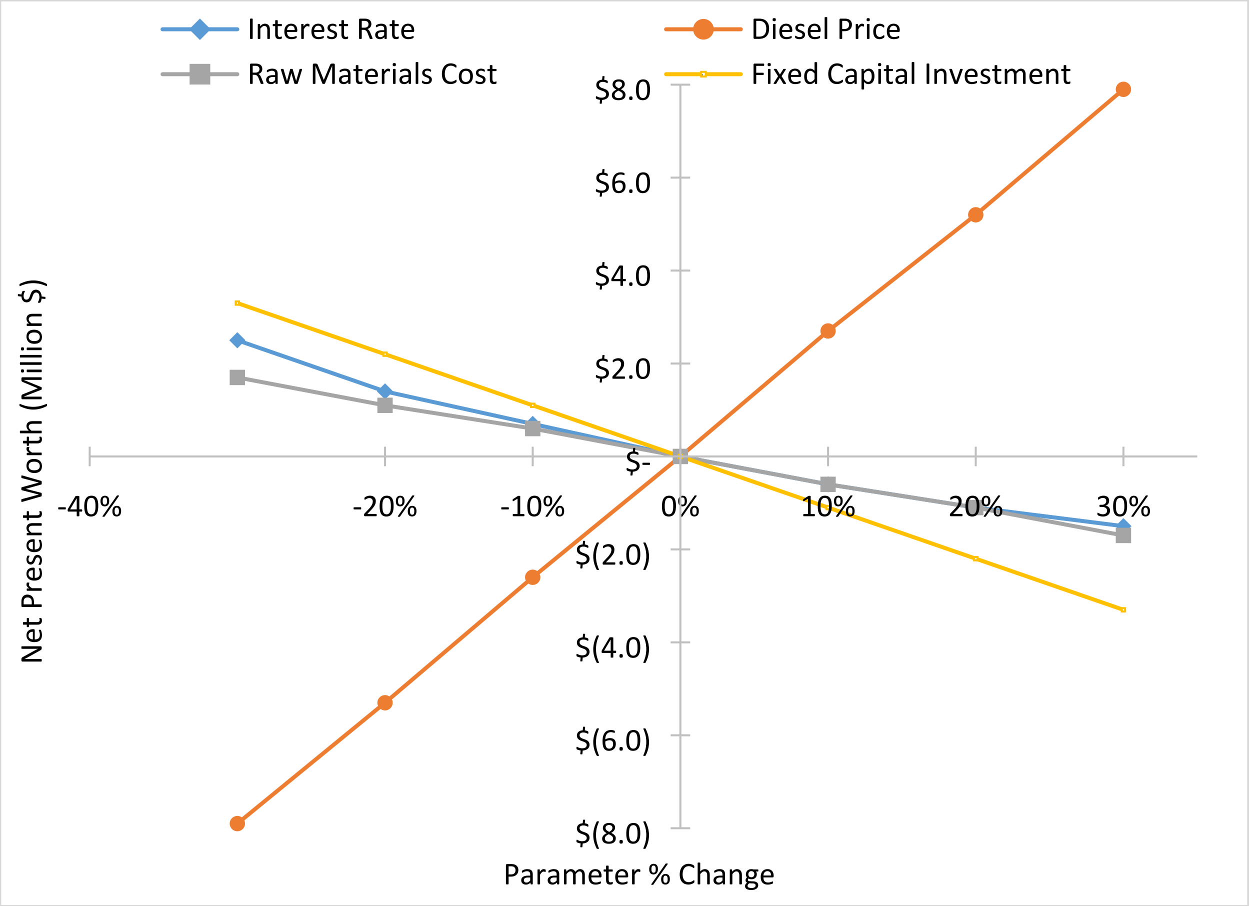

Fig. 7. Sensitivity analysis results. Base case is based on 15% interest rate, $3.24/gal diesel prices, $ 2.09 per MMBtu for LFG cost and total FCI of $8.5 million.

Comparison with power production

For comparison purposes, the tool LFGCOST-Web was used to compute the economics of producing power from the LFG [52]. Using the same economic assumptions as above, the capital cost requirement for an IC engine to produce power was estimated at $11.1 million, with a capacity of 6.7 MW power. At 6.0 ¢/kWhr, the NPV was estimated at -$2.4 million with a price of 10.5 ¢/kWhr required to breakeven. These calculations assumed that the LFG was free of cost. Thus in comparison with power production, this process appears to be much more attractive.

Conclusions

The laboratory studies show that reasonable yields of product liquid fuel can be obtained from LFG with the current state-of-the-art catalyst technology. The preliminary economic feasibility study indicate that the TriFTS process produced enough diesel to meet the fuel needed for the trucks used to haul the MSW to landfills. The breakeven cost for the process is estimated at \$3.24 per gallon and reduces to \$2.71 if the LFG is assumed to be free. However, if the diesel is sold, its certification as a renewable fuel can yield substantial RIN credits (an additional \$2-\$3 per gal of diesel sold), which would make this process economically attractive.

Important factors that remain uncertain are: the catalyst performance over time and regeneration protocols, the effect of fluctuating LFG flow and its composition, and the uncertainties in the preliminary economic evaluation which can be as high as ±50% for the FCI. These can lead to variations in the final cost of manufacturing. Long term pilot plant studies are required to lower the uncertainty in the design and economic evaluation.

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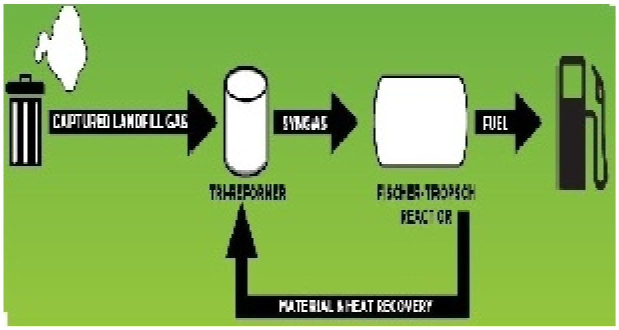

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