

# Advanced Syngas Upgrading Process for Conversion of Low-Rank Coals to Liquid Fuels

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**Abstract:** Syngas cleanup is a major challenge in any coal or biomass gasification application. A modified syngas cleanup process is under development to improve syngas from low rank coals for CTL (coal to liquids) applications. Novel steam reforming catalysts were developed to convert tars and light hydrocarbons and decompose ammonia in the presence of syngas contaminants such as H<sub>2</sub>S (< 500 ppm). Process goals are to improve syngas yield and H<sub>2</sub>:CO ratio while reducing water gas shift and downstream gas cleanup requirements. Laboratory reforming experiments were focused on developing information to support a techno-economic analysis using TRIG (transport reactor integrated gasifiers) or LURGI gasifiers. A CTL with carbon capture model was developed to compare the economics of the new process including the catalytic steam reforming to DOE (Department of Energy) baseline CTL. Reforming catalysts were developed that had high methane, tar, and ammonia conversion in presence of 90 ppm H<sub>2</sub>S. Higher concentrations of H<sub>2</sub>S affected conversion of methane but catalyst performance was fairly stable for the duration of testing. Results of modeling indicated that economics of the new process were nearly identical to the baseline CTL case, but greenhouse gas emissions for a given production of fuels were approximately 50% lower.

**Key words:** Steam reforming, CTL, gasifier, syngas cleanup, Fischer-Tropsch.

## 1. Introduction

Coal gasification is a complex, multi-step process that uses steam with air or oxygen to convert solid coal into its gaseous derivative components: H<sub>2</sub>, CO, H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub>, and contaminants. Recent advances in carbon capture have made it possible for CTL products to have comparable CO<sub>2</sub> emissions with its petroleum counterpart; with the potential to be even or below those levels when the feed is mixed with small amounts of biomass [1].

There are three main classifications of coal gasification technologies that are commercialized today: fluidized-bed, fixed-/moving-bed, and entrained-bed [2]. Fluidized-bed gasifiers use relatively narrow distribution of small particle sizes of coal that is fed into an inert bed which maintains a

uniform gasification temperature. The fluidized bed operates at lower temperatures and generally requires more reactive, low rank coals to achieve high conversions [3]. Fixed-bed gasifiers use preheated lumped coal that is fed from the top of the gasifier where air or oxygen and steam are fed from the bottom. Fixed-bed gasifiers consume lower amounts of O<sub>2</sub> but produce more tars and methane [3]. Entrained-bed gasification uses pulverized coal or coal water slurries under high temperatures (1,500-1,900 °C) which requires higher O<sub>2</sub> feed rates to maintain the reaction [3]. Transport reactor gasification (e.g., TRIG) is a recently developed gasification technology that was designed specifically for converting low-rank coals with low gas-solid transfer resistance and high gas-solid contact [2]. The TRIG system uses a limestone sorbent that is co-fed with the coal into the gasifier to remove the majority of the sulfur in situ down to levels as low as 100 ppmv which is substantially lower for the raw gas relative to

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other gasification technologies [3]. The temperature of operation is moderate and fairly high carbon conversion efficiencies of 97% to syngas are possible.

A major challenge in any coal gasification application is gas clean-up which represents 36-41% of the total plant cost when including the secondary application such as: SNG (synthetic natural gas), coal-to-methanol, or IGCC application [3, 4]. Additionally, the syngas derived from coal is typically lean in  $H_2$  relative to distillate fuels which have  $H_2:CO$  ratio of approximately 2:1.

The goal of this research was to develop and demonstrate potential economics of a high temperature catalytic steam reforming process that can withstand the severe contaminant conditions of a near-raw syngas derived from low-rank coal gasification with the objective to increase the yield and  $H_2:CO$  ratio while eliminating methane, ammonia, and tars from the process. Research was performed at the lab-scale using simulated low-rank coal syngas that contains methane, ammonia, as well as a tar surrogate to test the conversion efficiency and catalyst longevity.

Commercial application of steam reforming generally involves production of hydrogen. In 2010 there were 12 trillion standard cubic feet of  $H_2$  produced annually, primarily from steam reforming of natural gas. Typically all sulfur species in the natural gas are converted into  $H_2S$  via reduction or hydrolysis, then removed  $H_2S$  with  $ZnO$  scrubbing or other processes prior to methane/steam reforming over a Ni-based catalyst supported by  $Al_2O_3$  [5]. This reaction is typically carried out at temperatures over 700 °C, is thermodynamically more favorable with higher ratios of steam to carbon and at lower pressures [5]. Several studies have looked at novel methods for steam cracking of tar using Ni supported on dolomite [6, 7]. At 800 °C a nickel-ceria perovskite was shown to have favorable steam reforming activity of methane with high selectivities towards CO and  $H_2$  production [8]. Other studies have shown Ni hexaaluminates as a

high-temperature steam reforming or partial oxidation catalyst with relatively high carbon deposition resistance, especially in the presence of steam [9, 10].

The use of these catalysts faces several challenges; for example activity loss due to coking, thermal sintering, sulfur poisoning and metal sintering due to sulfur attack. The sulfur contaminants in hydrocarbon streams are present as  $H_2S$  or are converted to  $H_2S$  during high temperature reforming. Other forms of sulfur such as mercaptans and thiophenes also poison the catalyst. Most commonly used nickel oxide catalysts undergo rapid deactivation in presence of sulfur to unacceptable low level of methane or hydrocarbon conversion. Platinum and other noble metal catalysts also show high activity, and have slightly better susceptibility to sulfur, however, the rate of deactivation is still high. Also, platinum group catalysts are relatively very expensive to be used for large scale reforming applications.

Few attempts have been published for reforming catalysts developed to tolerate sulfur compounds in gaseous feeds. NexTech developed a magnesium nickel silicate catalyst that was tolerant to 10-20 ppm  $H_2S$  in the feed [11]. A nickel containing hydrotalcite dry reforming catalyst is described in US patent 6,953,488 [12] with 47% to 76% conversion of methane with a “low concentration of  $H_2S$  in the feed,” but no results for steam reforming are presented.

## 2. CTL (Coal to Liquids) Process under Development

Fig. 1 shows a process that converts low-rank coals (i.e., sub-bituminous and lignite) into distillate, hydrocarbon fuels using four main processing steps: gasification, clean up, syngas upgrading, and Fischer-Tropsch synthesis. This process begins by feeding steam, low-rank coal, and oxygen into a gasifier (e.g., TRIG or Lurgi’s FBDB (fixed-bed dry-bottom)) to produce a raw syngas which contains hydrogen, carbon monoxide, methane, carbon dioxide; trace contaminants: acid halides, mercury, phosphorous,

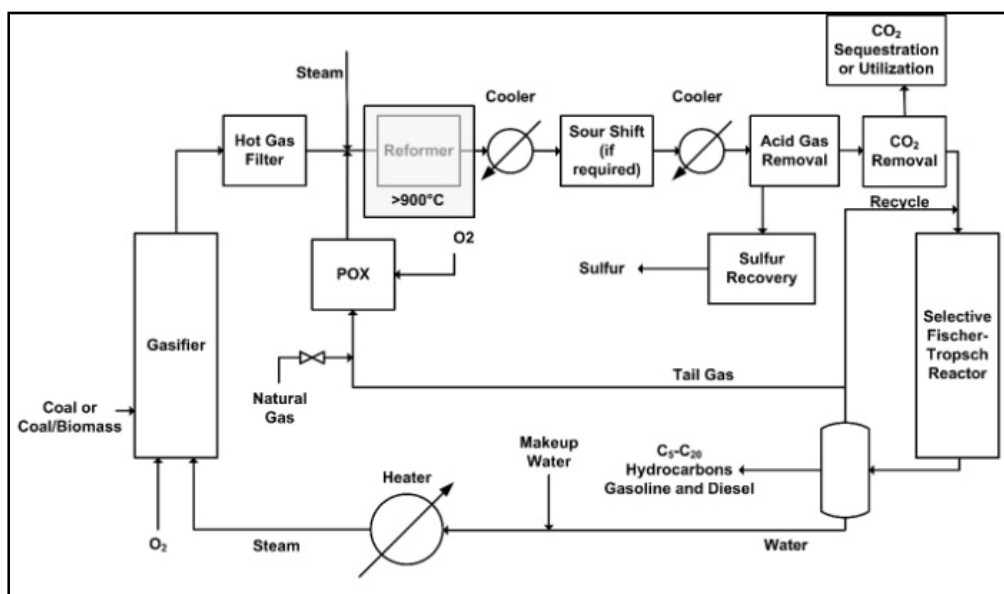


Fig. 1 Simplified flow diagram of CTL including new reforming process.

antimony, cadmium, hydrogen selenide, and arsine ( $\text{AsH}_3$ ); in addition: tar, particulates, ammonia, and sulfur ( $\text{H}_2\text{S}$ ,  $\text{COS}$ ) that are at or near percentage levels. Removing these contaminants is required to meet emission regulations for power generation as well as to prevent catalyst deactivation in the FT (Fischer-Tropsch) reactor. If a TRIG gasifier is used it would also require feeding limestone sorbent into the gasifier and remove the majority of sulfur from the syngas.

An acid halide sorbent is fed to the raw syngas prior to the hot gas filter which removes the remaining particulates and spent sorbent. Following hot gas filtration is a high temperature ( $> 900\text{ }^\circ\text{C}$ ) catalytic steam reforming step to convert the ammonia, methane, and tars into syngas which increases the  $\text{H}_2:\text{CO}$  ratio and eliminates these hydrocarbon and ammonia by-products from the syngas. Development of a catalyst that is stable under the severe deactivating conditions of a near-raw low rank coal (or coal-biomass) syngas containing tars, ammonia and methane is the focus of this proposed project. The high steam feed rates to the gasifier to produce higher  $\text{H}_2:\text{CO}$  ratios in the raw syngas also result in higher  $\text{CH}_4$  formation which are produced on a 3:1 ratio in

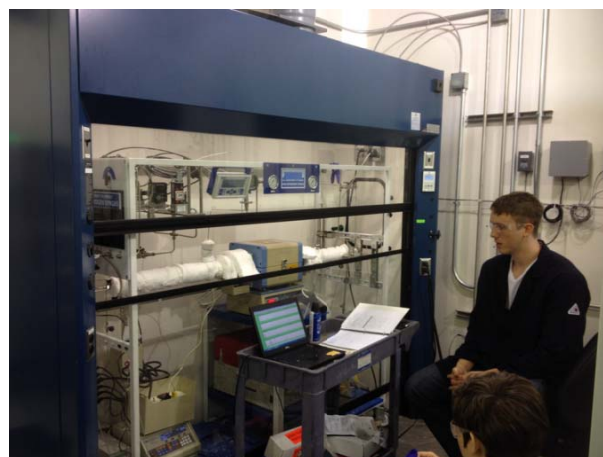
this reaction. Catalytic partial oxidation of light hydrocarbons produced upstream (i.e., Fischer-Tropsch derived  $\text{CH}_4$  and LPG) will further increase the  $\text{H}_2:\text{CO}$  ratio of the syngas; additionally, the heat generated from the partial oxidation step will be sufficient to maintain the temperature required for steam reforming which is endothermic. After cooling, the syngas can be subjected to an optional sour shift if needed for  $\text{H}_2:\text{CO}$  ratio adjustment. It is then desulfurized and further cleaned using conventional technologies followed by amine-based  $\text{CO}_2$  capture. Optionally the gas could be treated with warm gas cleanup technology such as that being developed by Research Triangle Institute under a cooperative agreement with the DOE to investigate the optimum sorbent-condition combinations. This technology has been successfully tested using a slip stream at the Eastman Chemical Plant's coal-to-chemical gasifier in Kingsport Tennessee [13]. The  $\text{H}_2:\text{CO}$  syngas is then fed to a FT reactor, upgrading, and separation section which maximizes the yield to liquid transportation fuels. The light hydrocarbons are recycled to the POX (partial oxidation) reactor unit to provide high quality heat for the steam reforming and to further increase the overall yield to liquid transportation fuels.

The H<sub>2</sub>:CO syngas is then fed to the selective FT reactor which maximizes the yield to liquid transportation fuels by making a wax-free product while maintaining relatively low yields to light hydrocarbons (C<sup>4</sup> < 25%) without needing an additional hydrocracking step. This technology is being developed by Chevron Corporation [14-17] and demonstrated by Southern Research under cooperative agreements with the Department of Energy. The FT liquids are passed to the distillation column and are separated into their respective fractions: light hydrocarbons (CH<sub>4</sub>, LPG), naphtha, jet, and diesel. The light hydrocarbons are recycled to the POX unit to provide high quality heat for the steam reforming and to further increase the yield to liquid transportation fuels.

### 3. Experimental

As mentioned previously, the process is enabled by the development of contaminant (particularly sulfur) tolerant reforming catalysts. Southern constructed a laboratory scale microreactor version (Fig. 2) of the catalytic steam reforming process with capability of controlling the flow rate, temperature, and pressure of simulated syngas to perform studies of a series of catalysts found in the literature in addition to some developed by Southern. Simulated syngas compositions were developed based on information found in Refs. [18, 19] and are summarized in Table 1. Three mass flow controllers (Brooks Instruments) were utilized to control the flow rate of hydrogen, nitrogen, or simulated syngas approximating either Lurgi or TRIG gasifiers except with varying H<sub>2</sub>S concentrations. In addition to purging as necessary, nitrogen was also used to provide a setpoint for the Equilibar back pressure regulator that controls reactor pressure.

Toluene was supplied as a tar simulant using a Teledyne Model 100DM Syringe pump equipped with their ISCO controller. Water (for steam) was supplied with an Eldex Optos Model 1LM metering pump. The toluene and water were mixed with the syngas mixture and vaporized in a static mixer prior to being fed to the tubular catalytic reactor purchased from MTI Corporation. Temperature was controlled by their OTF-1200X single zone programmable tube furnace. A Julabo FP 35 chiller is then used to cool and condense water out of the syngas exiting the reactor prior to online analysis of the remaining gas using an online gas chromatograph purchased from SRI Instruments, a modified MG3 configuration of their 8610 GC. Data from SRI's PeakSimple software were periodically downloaded into a spreadsheet to calculate methane, tar, and ammonia conversion as well as the relative changes in CO, H<sub>2</sub>, and CO<sub>2</sub>. Pressure was measured using an Omega DPG409-500G digital pressure gauge. The entire system was installed in a walk-in fume hood for all experiments conducted with H<sub>2</sub>S concentrations greater than 90 ppm. Catalysts were loaded in the center of the reactor mixed with inert diluent of the same



**Fig. 2** Photograph of laboratory reforming microreactor system.

**Table 1** Simulated syngas compositions of coal gasification.

	H <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub> O	H <sub>2</sub> S	NH <sub>3</sub>	Tar
TRIG-lignite	29.2%	34.3%	13.6%	2.5%	18.9%	100-250 (ppm)	28%	10%
Lurgi's FBDB-lignite	18.7%	7.5%	15.7%	5.2%	51.6%	29%	58%	41%

particle size with additional diluent to fill the remaining space on either side of the catalyst.

#### 4. Experimental Results

An initial series of short experiments was conducted to demonstrate that the measured effects were from the catalysts compared to inter diluent or other factors. Methane and tar conversions were measured for the empty reactor, the reactor filled with diluent only, and with a catalyst. Fig. 3 shows a summary of screening experiments conducted with 35 ppm  $H_2S$  for a number of catalysts plus the blank reactor and the inert diluent. Fig. 4 shows two experiments conducted with catalyst 1.1 with the  $H_2S$

concentration at 35 and 90 ppm. Increasing the  $H_2S$  concentration had little effect on stability of the catalyst. Fig. 5 shows two experiments conducted with 500 ppm  $H_2S$ . Although the conversions were much lower than that observed at 90 ppm, the performance was fairly stable, indicating that the catalysts were resisting poisoning.

#### 5. Modeling, Economic, and Lifecycle Analysis

To assess the steam reforming technology, several techno-economic and life-cycle analyses were conducted comparing a plant featuring the sulfur tolerant steam reformer and a base case without the technology.

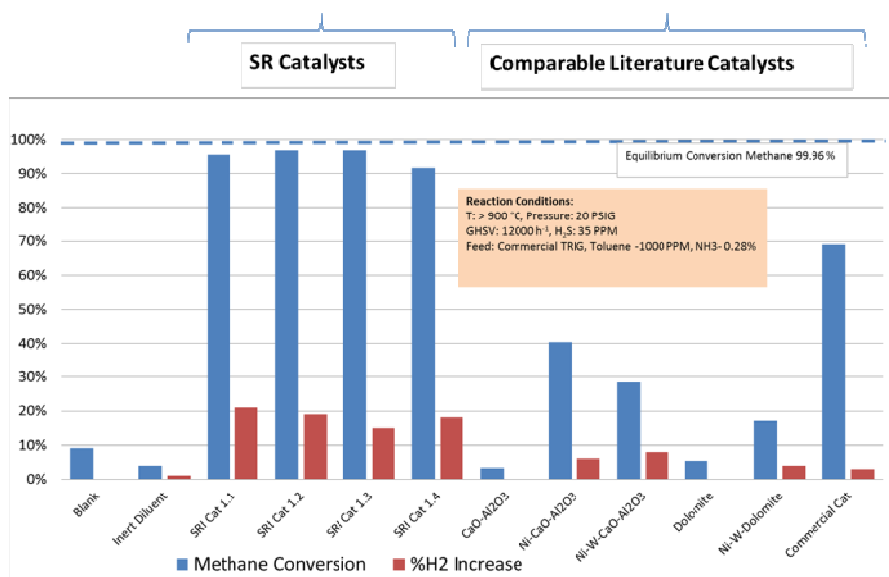


Fig. 3 Summary of catalyst tests with 35 ppm  $H_2S$ .

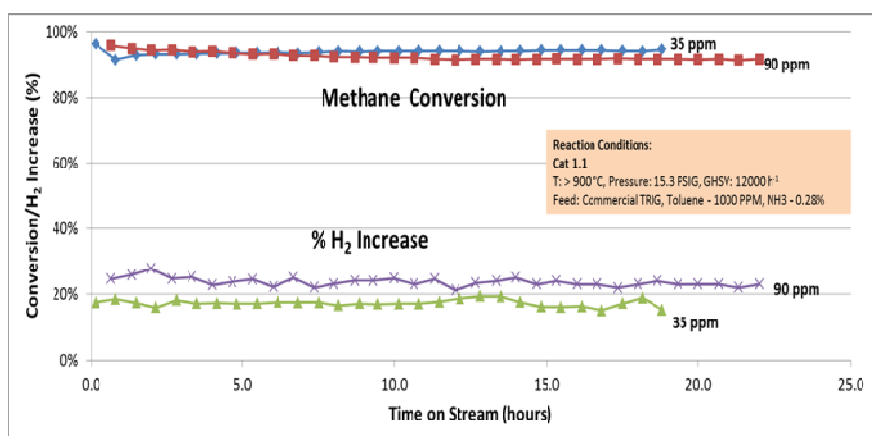


Fig. 4 Catalyst performance at 35 and 90 ppm  $H_2S$ .

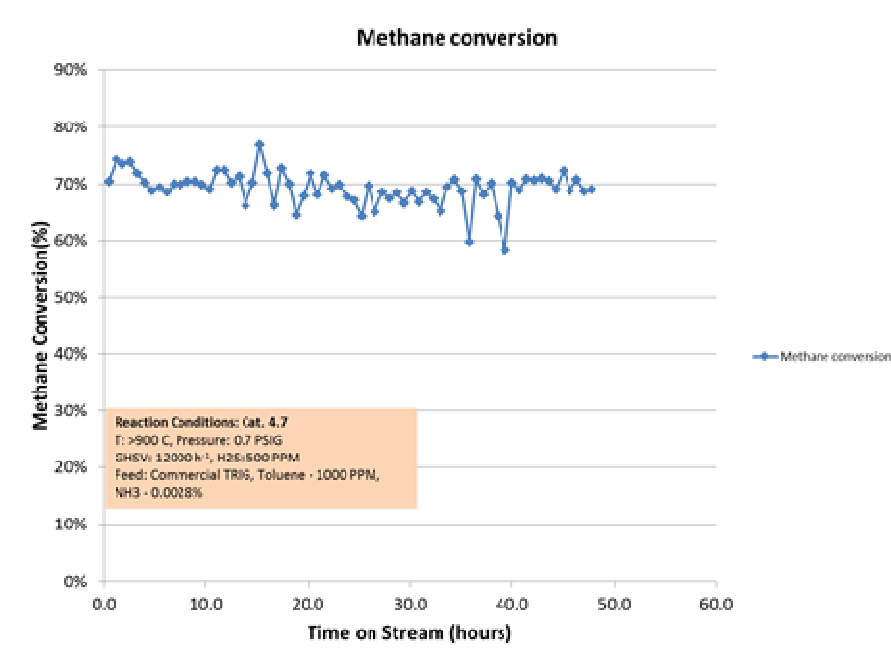


Fig. 5 Catalyst performance at 500 ppm H<sub>2</sub>S.

Table 2 Summary of FT production costs.

Total costs (\$1,000)	CTL base	Modified process
Overnight cost	\$5,858,852	\$5,625,013
Annual fixed O/M	\$190,000	\$184,000
Annual variable O/M (90% CF)	\$132,000	\$120,000
Annual feedstock (90% CF)	\$231,000	\$170,000
Annual power credit	-\$164,000	\$21,000
Cost of production/barrel	\$137.48	\$144.87
Barrels/day FT-liquid	49,996	49,996

An analysis was conducted by Nexant Inc. on a CTL plant using the TRIG gasifier. The primary comparison case for the steam reformer is based on the Department of Energy's National Energy Technology Laboratory's cost and performance baseline reports for CTL. An ASPEN Plus model simulation was generated to replicate the mass balance found in the NETL report, except that the single Shell gasifier in the DOE report was replaced with five TRIG gasifiers to provide the same liquid output (50,000 bpd). The simulation for the proposed new process was built by simply adding in the steam reforming block, POX reactor, and associated utilities. Utilizing the mass balances Nexant used the NETL reports as a guide for their TEA and LCA analysis. Table 2 shows a comparison of costs for the baseline

and modified CTL processes. The selective FT catalyst mentioned previously was not included in these analyses to allow for a direct comparison of the reforming process to DOE baselines.

As such, the simulation of the steam reformer was configured to produce syngas that closely matches the basecase in composition. To match the basecase output in the FT reactor it was necessary to produce syngas with a hydrogen to carbon monoxide ratio close to one, this required that the steam reformer was operated without the addition of steam. While this is not a common way to operate a steam reformer, it did, however, allow the simulation of the FT reactor to be simplified and provided a close comparison.

The POX/steam reformer's conversion of the light hydrocarbons to more syngas and CO<sub>2</sub> reduced the

**Table 3 Summary of lifecycle CO<sub>2</sub> emissions.**

	Base case (kg CO <sub>2</sub> e/barrel)	Modified case including POX/reformer (kg CO <sub>2</sub> e/barrel)
Upstream PRB Coal	100.0	73.6
PRB coal gasification	1,316.6	969.0
Sequestered CO <sub>2</sub>	-754.0	-598.0
Transportation of fuel	2.6	2.6
Electricity	-4.4	0.6
Produced fuel	-436.3	-436.3
Combustion of fuel	436.3	436.3
<b>Total emissions</b>	<b>660.8</b>	<b>447.8</b>

methane slippage from the gasifier to downstream nodes. This additional CO<sub>2</sub> produced was then captured and sequestered improving the carbon capture rate for the modified case to over 90%, while the basecase was not able to match this performance metric. The conversion of light hydrocarbons and tars to H<sub>2</sub> and CO by the POX/reformer improved the overall coal conversion efficiency and reduced the amount of coal required to produce 50,000 bpd of FT liquids. However, without the light hydrocarbons in the tail gas the energy content and volume of the tail gas was reduced which meant there was insufficient power being generated and the modified case became a net importer of electricity compared to the basecase which produced an excess of power.

Therefore, several key systems in the modified case had to be resized. The size of the air separation unit and carbon dioxide capture and sequestration equipment were all increased in size, while the coal feeding and power generation equipment were reduced in size relative to the base case. With the addition of the POX/reformer and the changes in equipment size the modified case had a slightly higher capital equipment cost, but lower O/M costs resulting in a 5.4% increase in per barrel cost for the modified case as seen in the table above.

Given that the liquid production for both cases remains the same, the downstream contributions are equivalent. However, the modified process provides a significant advantage over the basecase in feedstock avoidance. The upstream emissions associated with

the coal, the emissions released from the power generation system, and the lower carbon capture rate increase all contribute to a 47.5% higher CO<sub>2</sub> equivalent (CO<sub>2</sub>e) life cycle emission rate for the basecase when compared to the modified case. The breakdown of the contributing factors can be found in the table above.

## 6. Conclusions

A process is under development to improve syngas from low rank coals for CTL applications. Novel steam reforming catalysts with strong resistance to H<sub>2</sub>S poisoning were developed and demonstrated for up to 40 hours. Although overall economics for the process are not competitive compared to current oil prices, a techno-economic analysis developed for the process indicated near equal economics compared to baseline CTL processes with a large decrease in greenhouse gas emissions for equivalent FT liquids yields.

## 7. Future Work

Further tests of the catalysts developed will be conducted for extended periods of time, ideally thousands of hours. Techno-economic modeling will be expanded to hybrid cobalt-zeolite catalysts that minimize or eliminate produce upgrading for normal FT processes.

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