Small-Scale Coal-Biomass to Liquids Production Using Highly Selective Fischer-Tropsch Synthesis

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Abstract

The research project advanced coal-to-liquids (CTL) and coal-biomass to liquids (CBTL) processes by testing and validating Chevron's highly selective and active cobalt-zeolite hybrid Fischer-Tropsch (FT) catalyst to convert gasifier syngas predominantly to gasoline, jet fuel and diesel range hydrocarbon liquids, thereby eliminating expensive wax upgrading operations The National Carbon Capture Center (NCCC) operated by Southern Company (SC) at Wilsonville, Alabama served as the host site for the gasifier slip-stream testing/demonstration. Southern Research designed, installed and commissioned a bench scale skid mounted FT reactor system (SR-CBTL test rig) that was fully integrated with a slip stream from SC/NCCC's transport integrated gasifier (TRIG^{TM}). The test-rig was designed to receive up to 5 lb/h raw syngas augmented with bottled syngas to adjust the H_2/CO molar ratio to 2, clean it to cobalt FT catalyst specifications, and produce liquid FT products at the design capacity of 2 to 4 L/day. It employed a 2-inch diameter boiling water jacketed fixed-bed heat-exchange FT reactor incorporating Chevron's catalyst in Intramicron's high thermal conductivity micro-fibrous entrapped catalyst (MFEC) packing to efficiently remove heat produced by the highly exothermic FT reaction.

Two slipstream test campaigns were conducted. The first test demonstrated test-rig design productivity but had to be stopped prematurely due to a reactor heater failure. The second test was run for over 320+ hours including 70+ hours with Powder River basin (PRB) coal-derived syngas and 70 + hours with 80 % PRB coal and 20 % biomass-derived syngas. Ground hardwood pellets were used as the biomass fuel. Smooth operation with a seamless switch between various sources of syngas/fuel was achieved successfully demonstrating the design production rate of >> 2 L/day with about 75 % carbon selectivity to liquids. Efficient heat removal and hydrocarbon productivities more than 4 fold higher than conventional catalysts were demonstrated. The liquid product produced was nearly wax-free. The minor catalyst deactivation that was observed over the duration of the test was linked to traces of sulfur in the gas accumulating on the catalyst.

Comparative analyses of products from the CTL test with 100 % PRB coal and CBTL test with 80 % PRB coal and 20 % ground wood pellets did not show significant differences between the productivity, selectivity, and distribution of liquid products. Preliminary technical and economic analysis (TEA) indicated that there was a potential for about 7% capital cost and 5 % product cost reduction due to the use of a high activity/selectivity catalyst and elimination of wax upgrading, but competition with petroleum-based liquids would require collective improvements/cost reductions in all other major CTL/CBTL plant unit operations as well. Addition of biomass to coal had the potential of reducing the carbon foot print of CBTL compared to CTL and to bring it closer to the carbon foot print of petroleum-based fuel production processes.

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Executive Summary

As the United States continues to further improve energy security and decrease reliance on foreign oil sources, liquid transportation fuels from coal and biomass have the potential to impact the domestic transportation fuel markets. Large-scale CBTL process (with carbon capture) using coal mixed with a moderate amount of biomass is an attractive option. However, cost reductions and efficiency improvements are needed in every major and minor unit operation associated with the CBTL process to increase its market acceptance and for the process to realize its full potential. This project aims to demonstrate reduction in the cost of two key unit operations of CBTL: the Fischer-Tropsch (FT) synthesis and FT product upgrading and evaluate the impacts of the addition of biomass to coal at moderate levels on product characteristics and carbon foot print compared to petroleum based fuels, and economics of CBTL processes compared to coal only to liquids (CTL).

A 16ft x 8ft x10ft skid-mounted CBTL reactor system (SR-CBTL test rig), designed for production of 4 liter/day hydrocarbon liquids, was commissioned at the National Carbon Capture Center (NCCC) and tested for economical and environmentally-sustainable conversion of coal-biomass derived synthesis gas (syngas) to preferred hydrocarbon range (C_5 to C_{20}) transportation fuels by the FT process chemistry. The syngas was derived from gasification of coal and biomass in the large pilot-scale transport gasifier (TRIG^{TM}) at the NCCC gasifying 4000 lb/h of coal with 20 wt % biomass. The project participants included Southern Research as the project lead, Chevron Energy Technology Company (Chevron) as the FT catalyst supplier, Intramicron as the heat exchange reactor packing supplier, and Nexant for assisting with the required techno-economic analyses (TEA).

Chevron's patented hybrid cobalt-zeolite FT catalyst with exceptionally high productivity (>4 times conventional FT catalysts) and selectivity (>75 %) for gasoline, jet fuel, and diesel range hydrocarbons was used. Intramicron's micro-fibrous entrapped catalyst (MFEC) media was used to support Chevron's catalyst in the FT reactor to manage the heat of reaction and to minimize heat transfer limitations. The thermally conductive catalyst support allowed scale-up using larger diameter (2.0 inch) fixed-bed FT reactors compared to pellet testing in ½ inch reactors at Chevron. A thermo-syphon closed loop boiling water jacket designed by SR was used to remove the heat from the system to maintain nearly isothermal conditions both radially and axially.

During a typical run with gasifier syngas, bottled gases were fed first to the FT reactor to reach a steady state. Then gasifier syngas was brought in to replace a portion of the bottled syngas as follows. Typically, a 3 to 5 lb/hr raw/warm syngas slip stream from the air blown NCCC TRIG^{TM} gasifier was desulfurized using a sorbent/catalyst system that removed both H_2S and COS. The gas was then chilled and scrubbed to remove heavy hydrocarbons and ammonia. It was then compressed to the required FT pressure, mixed with H_2 and CO from bottled gases, as indicated above. This was done to increase its H_2/CO ratio to 2 and enrich it to simulate an oxygen-blown gasifier. The mixed gas (gasifier syngas and bottled syngas) was then sent to a series of guard beds for final polishing. It then entered the jacketed 2 inch diameter fixed-bed FT reactor with a water-based thermo-syphon heat removal system. The run began with activation of the catalyst in-situ followed by slow increase of temperature and pressure to the desired operating conditions. Once the catalyst reached steady state using bottled syngas, a portion of the bottled syngas was replaced by gasifier syngas. Gasifier syngas using coal was used first followed by gasifier syngas using coal + biomass.

Two slipstream test campaigns were conducted. The first test demonstrated test-rig design productivity but had to be stopped prematurely due to a reactor heater failure. The second test was run for over 320+ hours including 70+ hours with Powder River basin (PRB) coal-derived syngas and 70 + hours with 80 % PRB coal and 20 % biomass-derived syngas. Ground hardwood pellets were used as the biomass fuel. Smooth operation with a seamless switch between various sources of syngas/fuel was achieved successfully demonstrating the design production rate of >> 2 L/day with about 75 % carbon selectivity to liquids. Efficient heat removal and hydrocarbon productivities >>0.7 g/g catalyst/h were demonstrated. In comparison, a conventional FT catalyst has hydrocarbon productivities that are generally less than 0.2 g/gcatalyst/h. The liquid product produced was nearly wax-free. Comparative analyses of products from the CTL using 100 % PRB coal and CBTL test runs using 80 % PRB coal and 20 % ground wood pellets did not show significant differences between the productivity, selectivity, and distribution of liquid products. The small catalyst deactivation that was observed over the duration of the test was linked to traces of sulfur in the syngas accumulating on the catalyst. Sulfur levels of up to 164 ppmw were found on the used catalyst. Considering that sulfur is a strong poison to cobalt catalysts, the Chevron cobalt-zeolite hybrid catalyst exhibited significant resistance to sulfur.

Preliminary technical and economic analysis (TEA) indicated that there was a potential for about 7% capital cost and 5% product cost reduction due to the use of a high activity/selectivity catalyst and elimination of wax upgrading, but competition with petroleum-based liquids would require collective improvements and cost reductions in all other major CTL/CBTL plant unit operations as well. Addition of biomass to coal had the potential of reducing the carbon foot print of CBTL compared to CTL and to bring it closer to the carbon foot print of petroleum-based fuel production processes.

In conclusion, Southern Research has developed a fully functional CBTL test-rig and installed it on a slip stream alongside a large pilot-scale gasifier at NCCC that is a candidate for scale up for commercial operation. SR's test-rig has demonstrated excellent heat management capability. The testing verified the expected Chevron catalyst results of hydrocarbon productivity and solid wax-free product. Sulfur in the coal and/or coal + biomass syngas was the primary contaminant that was detected on the used catalyst and was potentially responsible for the slight deactivation. Even so, the catalyst exhibited significant resistance to potential sulfur poisoning. Other forms of potential sulfur compounds besides H2S and COS such as mercaptans, sulfides and thiophenes should be evaluated in the syngas. Following the development and implementation of techniques to completely remove both inorganic and organic sulfur compounds in syngas, a long-term slip stream test (500-700 hours) needs to be conducted to verify catalyst performance and long-term stability, and to provide sufficient data for scale up. To enable design of pilot and demonstration scale FT systems, a model should be developed using the data obtained for larger diameter (up to 6 inch) fixed bed FT reactors with the Chevron catalyst and MFEC packing. Based on this model, a technology transfer package should be prepared to attract industry to participate in scale up and demonstration of the technology.

Introduction

As the United States seeks to further improve energy security and decrease reliance on foreign oil sources, liquid transportation fuels from coal and biomass have the potential to significantly impact the domestic transportation fuel markets. Environmental mandates such as renewable fuel standard (RFS-2) require the production of significant amounts of transportation fuels from renewable sources such as biomass. Coal can be converted to transportation fuels via CTL process employing gasification-FT followed by wax hydrotreating, but these fuels do not count towards meeting the RFS-2 requirements.

Renewable fuels that can be produced from biomass for blending into transportation fuels include biodiesel and ethanol. But, these options by themselves are unattractive and cannot meet the RFS-2 requirements. Biomass can also be converted to a bio-oil using pyrolysis or liquefaction that can potentially be upgraded to transportation fuels in a petroleum refinery. Bio-oils however are highly acidic, have a very wide carbon number distribution, have significant stability issues due to the presence of large amounts of oxygenated acidic compounds, and require extensive separation and hydrotreating for stabilization and conversion to transportation fuels. Biomass can also be converted via gasification-FT followed by wax hydrotreating to diesel in a manner similar to coal. The problem, however, is that biomass, though abundant, is not only a low energy density fuel in contrast to coal, but also lacks the harvesting, collection and transportation infrastructure for large scale biomass to liquids (BTL) production.

Large-scale CBTL process (with carbon capture) using coal mixed with a moderate amount of biomass is an attractive option. However, initial markets must be established to demonstrate impacts and acceptance of CBTL fuels. Although, there are several CTL and CBTL projects that have been proposed for future development, none are currently in production in the U.S. A major barrier to widespread deployment is capital cost associated with these plants.

This project aims to reduce the cost of CTL and CBTL processes based on gasification/ FT synthesis by maximizing the production of gasoline and diesel range hydrocarbon liquids and eliminating the undesirable production of wax that requires expensive upgrading operations. The proposed CBTL technology uses a proprietary high activity and selectivity cobalt-zeolite hybrid catalyst from Chevron in a fixed-bed catalytic reactor system with a novel, highly efficient, heat removal system that enables much higher hydrocarbon productivity per unit volume of reactor versus conventional high alpha FT catalysts. It has the potential to provide significant improvements over CBTL with conventional FT by eliminating the wax collection and upgrading step and thereby reducing the cost of transportation fuel production.

Objectives and Technical Approach

The overall objective of this Southern Research (SR) project under cooperative agreement DE-FE0010231with the Department of Energy/ National Energy Technology Laboratory (DOE/NETL) is to design, commission, and test a coal-biomass to liquids (CBTL) reactor system for economical and environmentally-sustainable conversion of coal-biomass derived synthesis gas (syngas)to preferred hydrocarbon range (C_5 to C_{20}) transportation fuels by the Fischer-Tropsch process chemistry. The project aims to:

- Reduce the cost of CBTL processes based on gasification/FT synthesis by maximizing the production of gasoline and diesel range hydrocarbon liquids using a proprietary catalyst and eliminate the undesirable production of wax that requires expensive downstream upgrading operations;
- Evaluate the impacts of the addition of biomass to coal at moderate levels on product characteristics, carbon foot print compared to petroleum based fuels, and economics of CBTL processes compared to coal only to liquids (CTL).

The technical approach consisted of the production of 2 to 4 liters/day of FT liquid in Southern Research’s scalable skid-mounted bench-scale reactor system (SR-CBTL test-rig) using a slip stream of coal or coal/biomass gasifier syngas. The syngas was derived from gasification of coal and biomass in a large pilot-scale gasifier gasifying 4000 lb/h of coal with 20 wt % biomass. The project participants included Southern Research as the project lead, Chevron Energy Technology Company (Chevron) as the catalyst supplier, Intramicron as the heat exchange reactor packing supplier, and Nexant for assisting with the required techno-economic analyses (TEA) and life cycle analysis (LCA). The slip-stream testing host site was provided by the National Carbon Capture Center (NCCC) operated by Southern Company (SC) at Wilsonville, Alabama where the pilot-scale gasifier is located.

The project objectives were accomplished by:

- Designing, fabricating and commissioning the skid-mounted bench scale FT reactor system (SR-CBTL test-rig) for producing liquids at design rate from a gasifier slip stream
- Coordinating the slip stream testing with scheduled coal and coal-biomass gasification runs by SC using the pilot-scale TRIG^{TM} system at NCCC;
- Feeding a slip stream of the produced syngas to the bench scale reactor containing the novel selective FT catalyst to produce predominantly C_5 to C_{20} gasoline and diesel range hydrocarbons liquids with high activity and >75 % carbon selectivity;
- Evaluating the impacts of moderate (up to 20 %) biomass addition to TRIG^{TM} system operation, and FT liquid products; and
- Conducting preliminary TEA and LCA of the process

Technology Background and Description

CBTL Advantages and Capital Cost Limitations

Coal and biomass are two of the most plausible alternative fuels for replacing petroleum as a source of transportation fuels [National Research Council, 2009]. The total US oil consumption is >21 million barrels/day (Mbpd). About 14 Mbpd is used in the transportation sector with light duty vehicles accounting for about 9 Mbpd (138 billion gallons/year) [Energy Information Administration, 2009]. Oil resources are finite and alternative energy sources need to be developed. As the United States seeks to improve energy security and decrease reliance on foreign oil sources, CTL fuels have the potential to significantly impact the domestic transportation fuel markets. CBTL fuels have the potential to also do so and simultaneously positively impact lifecycle GHG emissions when compared to petroleum derived fuels. However, initial markets must be established to demonstrate impacts and acceptance of CBTL fuels.

One potential major customer is the U.S. Department of the Defense that desires to improve its environmental performance and is exploring options to reduce carbon emissions of the plants producing synthetic fuels to less than that of a conventional petroleum refinery on an energy content basis. To improve energy security and reduce costs, the U.S. Air Force has set a goal to supply 50% of its fuel requirements in the lower 48 States from domestic synthetic sources by 2016 [DOE/NETL, 2007].The U.S. Air Force has qualified its fleet on FT and other synthetic fuel blends, in anticipation of using biofuels or other domestically sourced fuels in its fleet for economic and energy security reasons. The U.S. Navy has also implemented similar programs and is pushing forward with the demonstration of its Great Green Fleet, operating on biofuel. The implementation of CBTL fuels will allow the USAF and Navy to rapidly meet the required production goals to support the agencies while remaining GHG negative compared to petroleum fuels.

As an alternative to oil, the US has an abundant supply of proven coal reserves that can last for over 100 years. The infrastructure for coal mining and supply is quite good because of its significant use to produce electricity. Coal is also competitive in price but increasing its use for converting coal to liquids (CTL) in addition to electricity is not sustainable due to increased CO_2 emissions that contribute to global climate change. Social acceptance is also an issue with increased coal use due to increased mining operations.

Compared to coal, biomass, an abundant resource, is a renewable CO_2 neutral fuel. A major barrier to increasing the use of biomass in BTL plants is the poor to non-existent infrastructure for harvesting and transporting biomass for large scale use. The availability of cellulosic (non-food) biomass or waste biomass for BTL plants is neither cheap nor abundant in a practical sense. It is estimated that with modern cultivating and harvesting techniques, sustainable cellulosic biomass resource can be increased to 550 million tons/year by 2020 [National Research Council, 2009].

CTL has been commercially available via the gasification/Fischer-Tropsch (FT) route for over 55 years. However, there are no commercial plants that make fuels and chemicals from coal in the US (except Eastman's coal to chemicals complex in Kingsport). This is due to a combination of several reasons including economics with respect to petroleum, high capital costs involved, and environmental and social acceptance. CTL can be commercially deployed but will not be until large scale carbon capture and storage (CCS) is commercially demonstrated.

There are no commercial BTL plants operating in the US. The Energy Independence and Security Act (EISA) of 2007 mandates increasing renewable fuels from sources such as biomass nearly 10-fold to >2.3 million barrels per day by 2022. This act has led to significant ongoing funding by the U.S. DOE to promote biomass to liquids (BTL) research, development, and demonstration. BTL plants may require significant Government incentives for CO_2 reductions before any private companies assume the risks to build them.

CBTL is attractive to develop since plants using 60 % coal and 40 % biomass can produce 4 Mbpd by 2020 at equivalent CO_2 emissions as petroleum without CCS. This is because the use of 40 % biomass reduces the impact of the total CO_2 emissions. Liquid fuels from biomass and coal have the potential to reduce petroleum fuel use and CO_2 emissions in the U.S. transportation sector over the next 25 years according to a recent study by the National Research Council [2009] that further indicates that CTL and CBTL plants are economically competitive with petroleum based plants as shown in Table 1.

Table 1. Comparison of $/barrel Gasoline Equivalent Cost (CCS implies 90 % CO_2 capture and storage)*

	Without CO_2 price	With $50/metric ton CO_2
CTL	65	120
CTL-CCS	70	90
Crude oil at $60 per barrel	75	95
Crude oil at $100 per barrel	115	135
CBTL	95	120
CBTL-CCS	110	100

*Adapted from [1]

According to the NRC report, "A program of aggressive support for establishment of first-mover commercial coal-to-liquid transportation fuel plants and coal-and-biomass-to-liquid (CBTL) transportation-fuel plants with integrated geologic CO_2 storage will have to be undertaken immediately if commercial plants are to be deployed by 2020 to address U.S. energy security concerns and to provide fuels whose levels of greenhouse gas emissions are similar to or less than that of petroleum-based fuels."

A DOE/NETL published report also indicates advantages of CBTL with CO2 capture [DOE/NETL, 2009]. According to this report, with a minimum of 8 % by weight biomass feed and with CO_2 sequestration, CBTL process can produce fuels which are economically completive at crude prices above $93 per barrel and which have 20% lower Green House Gas (GHG) emissions than petroleum fuel.

However, further performance improvements and cost reductions in CBTL plants are needed to reduce investor risk in these plants that can cost over a billion dollars. Although, there are several CTL and CBTL projects that have been proposed for future development, none are currently in production in the U.S. Cost reductions/efficiency improvements are needed in every major/minor unit operation associated with the CBTL process to increase its market acceptance and for the process to realize its full potential.

Technologies Selected for CBTL Cost Reduction

This project aims to demonstrate reduction in the cost of two key unit operations of CBTL: the FT synthesis and product upgrading using a slip stream from the SC/NCCC TRIG^{TM} gasifier. Chevron's highly active and selective co-zeolite hybrid catalyst and a simple fixed-bed reactor design with efficient heat transfer using Intrmicron's micro-fiber packing have the potential to reduce the size and number of FT reactor tubes, and eliminate the product upgrading operation. The TRIG^{TM} facility at NCCC along with the bench-scale FT reactor system (SR-CBTL test-rig) employing Chevron's catalyst and SR-Intramicron's novel heat removal system was chosen because of its ability to scale results to commercial applications. The NCCC gasifier facility is large enough to give industry real-life data, yet small enough to be cost-effective as a test bed, including bench and pilot scale testing of innovative processes using syngas slipstreams. The use of the highly active/selective FT catalyst with an efficient heat removal reactor is believed to be a major step forward, reducing the number/size of costly unit operations to convert syngas to the desirable liquid transportation fuels, and improving system economics.

NCCC Gasifier

The NCCC gasification system operated by Southern Company (SC), with a nominal capacity of 4000 lb/h coal, features key components of an integrated gasification combined cycle (IGCC) plant. These include high pressure solids feed systems; a Transport Gasifier; syngas coolers; a particulate control device; continuous ash depressurization systems for ash cooling and removal; and a recycle syngas compressor. The process also accommodates a slipstream unit to test syngas conditioning technologies under various operating conditions. The project proposed here will utilize the existing slipstream from the transport gasifier and all available supporting infrastructure as the source of both coal and coal-biomass derived syngas.

The NCCC gasification process features the Transport Gasifier, a dry-feed, non-slagging fluidized bed gasifier, which operates at lower temperatures than other commercially available coal gasifiers. The gasifier has operated successfully on a wide range of fuels, including subbituminous, bituminous, and lignite coals as well as biomass fuel. Features of the Transport Gasifier include:

- Simple, well established design based on technology in use for 70 years;
- Equally effective gasification in either air- or oxygen-blown modes of operation;
- High reliability non-slagging design, which allows a 10- to 20-year refractory life;
- Operation without burners enhances reliability and minimizes maintenance requirements;
- Use of coarse, dry coal feed, which requires fewer and lower power pulverizers, and less drying;
- Cost-effective operation and high carbon conversion with high moisture/ash and low rank fuels;
- Excellent heat and mass transfer due to a high solids mass flux, with a solids circulation rate 80 to 100 times greater than the coal feed rate.

One of the goals of the NCCC is to increase fuel flexibility for advanced coal- fired power systems through feeder development and through gasifier operation with a wide variety of coals and biomass feedstocks. Since feeding biomass/coal mixtures into high pressure and high temperature environments is a major barrier to biomass utilization in advanced power generation systems, demonstration of reliable feed systems capable of feeding biomass/coal mixtures is needed so that biomass can be widely utilized. The NCCC has been developing a feed system capable of handling a wide range of fuels, including biomass – the Pressure Decoupled Advanced Coal (PDAC) feeder. The facility has used a variety of feedstocks, but now primarily uses Powder River Basin (PRB) coal, milled to 200-500 microns as the primary coal feedstock. The NCCC has also used pelletized hard wood successfully, with biomass sized between 500 and 800 microns.

The gasifier produces about 20,000 lb/h of raw syngas and the main slipstreamof 1500 lb/h is directed to the syngas conditioning unit (SCU). The SCU is a flexible slipstream facility that can accommodate multiple, small-scale tests, such as water-gas shift, hydrolysis, syngas conversion, desulfurization, and CO2 capture. The SCU consists of small reactor vessels, arranged to allow operation in series or in parallel, which accommodate a range of flow rates, temperatures, and pressures. In addition to testing with syngas when the Transport Gasifier is in operation, tests are conducted during plant outages using bottled gases. Syngas slipstreams ranging from 3 lb/hr to 500 lb/hr are available at the facility.

The gasifier typically runs two test campaigns each year, with research being performed on a variety of focus areas and also supporting the testing of novel technologies on the slipstream. The system typically operates 500-1000 hours per test campaign. These run times at the NCCC are sufficient for the CBTL tests described in this report.

Conventional FT Catalyst Technology

Fischer-Tropsch synthesis (FTS), originally discovered in Germany more than 85 years ago, is presently the preferred route for converting syngas (H_2 + CO) made from coal, biomass, or natural gas into a wide variety of hydrocarbons [Dry 1980, 1996; Anderson 1984, Adesina

1996; Jager and Espinoza 1995; van der Laan 2001]. For the production of liquid transportation fuels, carbon numbers in the gasoline and diesel range of C_5 to C_{20} are preferred. Unfortunately, conventional FTS is non-selective and results in a wide product slate ranging from C_1 to C_{60}+ hydrocarbons via chain growth polymerization reactions ($CO + 2H_2 \rightarrow -CH_2- + H_2O$). The hydrocarbon chain growth in FTS is dictated by the Anderson-Schulz-Flory (ASF) distribution parameter, α, typically ranging from 0.75 to 0.95. A catalyst with α of 0.9 or higher is preferred as it produces less gaseous hydrocarbons. Although this results in formation of significant amount of undesirable waxes (C_{21}+), production of undesirable light gases (C_1 to C_4) is minimized. The waxes are then subjected to mild hydrocracking/hydrotreating operations to convert them to the extent possible to desirable transportation fuel-range hydrocarbons (C_5 to C_{20}). Chevron's selective catalyst technology that this project is seeking to demonstrate for CTL and CBTL applications avoids these expensive downstream processing requirements by not producing the waxes while also producing low levels of light gases.

High α iron and cobalt based catalysts ($\alpha > 0.9$) are typically used for conventional FTS. Ruthenium based catalyst is also a potential choice for FTS but, due to its high cost, has not received much attention compared to iron and cobalt based catalysts. Although iron-based FTS was first to be commercialized by Sasol in 1955 for CTL, high α cobalt-based catalysts are the current commercial choice for FTS (for example the commercial natural gas-based Sasol and Shell FTS plants in Qatar) because of their higher activity, greater durability, higher attrition resistance, higher selectivity to alkanes, and much lower (near zero) CO_2 selectivity compared to iron. Cobalt-based high α catalysts are presently the preferred catalysts not only for natural-gas based FTS plants but also for commercial-scale CTL and CBTL processes with CO_2 capture. Commercial coal gasifiers produce a syngas with a H_2/CO mol ratio of <1 whereas cobalt catalysts require a syngas with a H_2/CO mol ratio of 1.8-2.1. For cobalt catalysts, the syngas is subjected to a sour shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) to adjust the H_2/CO mol ratio. The syngas is then cleaned and the CO_2 captured before FTS. Iron based catalysts possess the ability to process syngas with low H_2/CO ratio because the FTS reaction on iron catalysts is accompanied by shift that produces the H_2 needed for the FTS and CO_2 which can be captured downstream of FTS. However, iron catalysts produce significant levels of CO_2, and also more olefins compared to cobalt catalysts.

The advantages of cobalt catalysts (higher activity, very low olefin make, greater durability, higher attrition resistance and very low CO_2 selectivity) and the requirement for CO_2 capture for CTL and CBTL processes outweigh iron catalyst's advantage of not requiring a shift reactor. Thus iron based catalysts are not a serious contender for employment in large scale CTL and CBTL plants. However, currently available high α cobalt-based catalysts are non-selective and produce a slate of hydrocarbons ranging from C_1 to C_{60}+ that necessitates extensive downstream upgrading operations for the waxes produced. Also, the C_5 to C_{10} fraction (naphtha) produced has significant paraffins, a poor gasoline blend, and needs to be upgraded elsewhere. The FTS and wax upgrading section can account for as much as 35 % of the capital requirement of a CTL plant [Choi 1996]. Thus, reducing the size of FTS and eliminating the upgrading operations can contribute significantly towards reducing the cost of CTL and CBTL processes.

Chevron Hybrid Catalyst Technology

Chevron has developed and patented hybrid cobalt-zeolite and ruthenium-zeolite catalysts that exhibit exceptionally high selectivity to drop-in gasoline and diesel range hydrocarbons. Over 20 patents and patent applications have been issued or are pending covering various aspects of Chevron's catalyst technology [Chevron Corporation, private communication]. Some of these patents and patent applications are referenced here: Kibby et al. 2011a, 2011b, 2011c; Jothimurugesan et al. 2012. The catalysts have been prepared for fixed-bed applications as extrudates that can be used in a single 3/4 to 1-inch diameter reactor tube representative of the numerous tubes used in shell and tube configuration in commercial operation. Chevron's patents also cover fluidized-bed and slurry reactor applications. However, this project seeks to demonstrate the developed catalysts in larger 2 inch diameter fixed beds (with novel heat exchange capability as described in the next section) using actual syngas from the transport gasifier at NCCC. Chevron has tested their catalysts at lab-scale in small micro reactors using synthetic H_2-CO blends and has shown high activity and selectivity. Chevron is committed to scaling up and commercializing these catalysts as evidenced by the significant R&D investment they have already made and are continuing to make to further improve these catalysts.

As described in the referenced patents, the hybrid catalysts typically consist of FTS-active metals, cobalt and ruthenium, that carryout the FTS. These metals are combined with specially tailored zeolites that limit the products primarily to the C5-C20 range liquids. Although the concept of the hybrid catalyst is not new, with publications dating back to as early as 1980 [Fraenkel and Gates 1980; Bessel 1995; McMohan et al. 1987], as well as that are recent [Bao et al. 2011], attempts by others to develop these catalysts have not been systematic and has largely met with failure potentially due to excessive cracking by the zeolite, resulting in production of large amounts of light gases. Development of Chevron's hybrid cobalt catalysts uses their extensive knowledge in preparation and activation of FT catalysts and preparation of specially tailored zeolites.

As an example of high selectivity to gasoline and diesel range hydrocarbons and very low to negligible wax formation, FT experimental results for a Chevron cobalt hybrid catalyst containing 10 wt% cobalt, 0.25 wt% Ru, 72 wt% ZSM-5 and 18 wt % alumina are shown in Table 2 (Kibby et al. [2011c]). It is noteworthy that under the conditions of the test, there appears to be no catalyst deactivation up to 440 hours. Also, the selectivity to the desirable C_5 to C_{20} fraction is as high as 79%, and clear liquids are produced with essentially no wax formation .

The products formed from the Chevron cobalt hybrid catalyst have the potential for direct blending with gasoline and diesel without any further upgrading.

Table 2. FTS Performance of a Chevron Co-zeolite Catalyst (235^{o}C; H_2/CO= 1.6; 6000 scc/g.h)

Time on stream (h)	254	326	419	440
Pressure (atm)	10	10	15	20
CO conversion (%)	35.1	34.5	38.4	41.7
CH_4 selectivity (%)	12.6	12.6	12.3	11.9
C_2 selectivity (%)	1.7	1.7	1.7	1.4
C_3-C_4 selectivity (%)	10.8	11.1	8.9	7.9
C_5-C_{20} selectivty (%)	74.9	74.6	77.4	79.0
C_{21} + selectivity (%)	2	0	0	0

Intramicron Microfibrous Entrapped catalyst (MFEC)

Fixed bed reactors are much simpler to model, scale up, design, construct and operate compared to fluidized-bed or slurry reactors, and are generally the reactors of choice for most industrially important reactions. However, because the FT reaction is highly exothermic, heat transfer requirements typically limit the reactor diameter to 1 inch or less. These small diameter tubes result in very tall tubes and large number of tubes to house the required amounts of catalyst. And, when using even these narrow tubes, the FT reaction presents a substantial control challenge because of large temperature gradients axially across the catalyst bed. Complicated reactor designs, including fluidized-bed and slurry-phase reactors, are commonly employed to overcome these limitations; however, they are much more complicated and also do not scale down well.

For this project, Intramicron's microfibrous entrapped catalyst (MFEC) media was used to support Chevron's catalyst to manage the heat of reaction and to minimize heat transfer limitations. The media used was a thermally conductive, highly-porous, sintered non-woven support structure. Further details of the Intra micron's MFEC technology are available at www.intramicron.com.

Experimental Methods

SR-CBTL Test Rig

A rigorous design and process hazard analysis of the skid-mounted 2-4 liter/day SR-CBTL test rig in which SR and NCCC staff jointly participated, was carried out. The components of the CBTL test rig were then procured and assembly began in the SR high-bay pilot facility in Durham, NC. The test-rig during initial construction with a few of the vessels mounted at the SR pilot plant facility is shown in Figure 1. It had a footprint of 16 feet by 8 feet and a height of 8 feet.

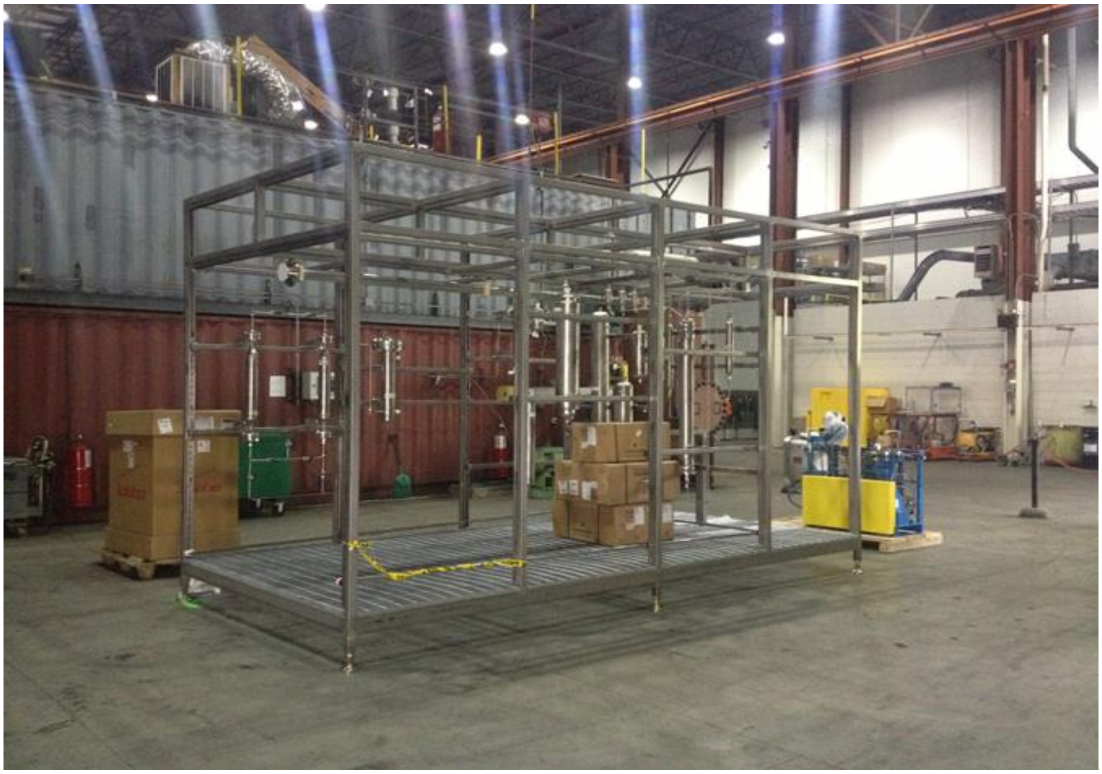

Figure 1. SR-CBTL test rig under initial construction at SR pilot plant

In parallel, plans were made in cooperation with NCCC personnel for the transportation, positioning and installation of the test rig at NCCC. The slip stream testing facility at NCCC is shown in Figure 2. After completing construction and commissioning the rig using nitrogen at SR, it was prepared, packaged and loaded on a flat-bed truck for shipment to the NCCC gasifier site in Wilsonville, Alabama. A 3D drawing of the test-rig showing the plans for syngas and utility connections is shown in Figure 3. After the test-rig arrived at NCCC in early January 2014, it was unloaded from the truck with the help of SC/NCCC personnel and equipment and positioned into its location as shown in Figure 4. Over the next 2 months, with the help of SC/NCCC staff and on-site contractors, all process and utility lines/wires including 480 V power, 120 V power, 24 V power, signal wires to control room trailer, analytical lines/wire

Figure 2. Slip-stream testing facility alongside the TRIG^{TM} gasifier at NCCC

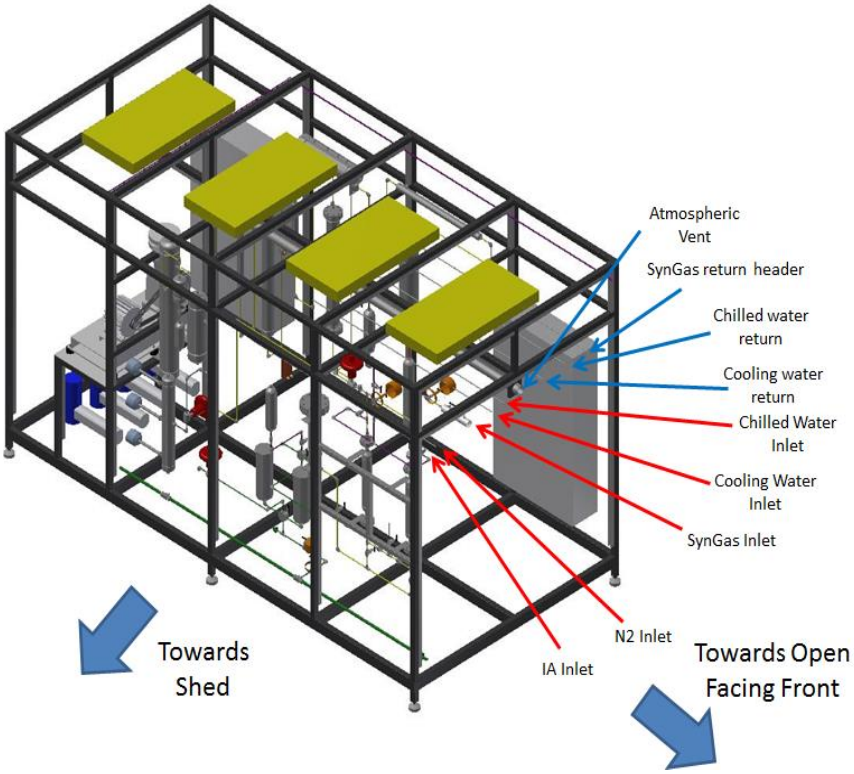

Figure 3. 3D FT skid drawing showing front and side views

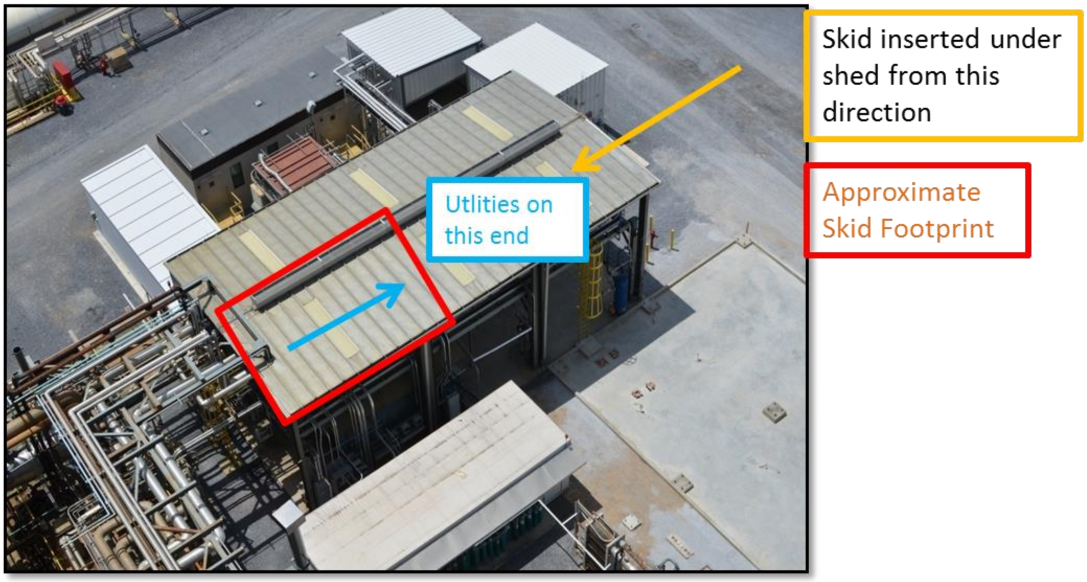

Figure 4. SR CBTL test-rig insertion route into NCCC slipstream shed

to/from analytical trailer, instrument air, chiller antifreeze, demineralized process water, cooling water, medium pressure nitrogen, hot nitrogen, hot syngas, bottled CO and H_2, process water drain, syngas return, and required process vents and relief vents were connected to unit. The entire unit was tested and commissioned in sections, including remote data acquisition, operation, and control. Sampling and analysis system including a continuous analyzer for controlling H_2/CO ratio in the feed and an online gas chromatograph was also commissioned. The system conformed to Class 1, Division 2 electrical classification. Fifty five tons of biomass pellets were procured in anticipation of the coal-biomass testing following the coal runs.

The electronic signals from the test-rig were sent to a control room trailer shown in Figure 4 for remote control and operation of the system. Lab View software was used to run the PLC program on a computer (human machine interface) in the control room. Feed gas and tail gas sample lines were connected to the analytical room trailer where the gas sampling system, SR GC system, and continuous CO/H2/CO2 analyzer were installed. The controls and heaters on the system were fully checked out to ensure proper operation. Finally the unit was pressure tested and insulated and was ready for operation.

Figures 5-8 are photographs of the SR CBTL test-rig taken from various angles. Figure 5 shows a front view that shows the rig has walk in and around capability. The raw syngas cleanup system is on the left, the compressor and guard beds are in the back, and the reactor and product collection traps are on the right along with the PLC panel. Figure 6 is a closer view of the reactor and product collector, and Figure 7 shows a close up of the gas cleaning system including the hot H_2S and COS traps, the heavy hydrocarbon/tar scrubber, ammonia scrubber, and a series of guard beds. Figure 8 shows a rear view showing the mass flow controller an d power panels, compressor, and scrubber water pumps.

A simple schematic of the installation of the CBTL test-rig is shown in Figure 9. The unit had the capability to run on bottled gas, syngas and a combination of both. During a typical run with gasifier syngas, bottled gases were begun first through the FT reactor to reach a steady state. Then gasifier syngas was brought in to replace a portion of the bottled syngas as follows. Typically, a 3 to 5 lb/hr raw/warm syngas slip stream from the air blown NCCC TRIG^{TM} gasifier was desulfurized using a sorbent/catalyst system that removed both H2S and COS. The gas was then chilled and scrubbed to remove heavy hydrocarbons and ammonia. It was then compressed to the required FT pressure, and mixed with H_2 and CO from bottled gases, as indicated above.

Figure 5. SR-CBTL test-rig in position at NCCC;walk-in and around capability; Hot sulfur trap on left; Purged PLC Enclosure on Right

Figure 6. Guard beds, FT reactor and product collection

Figure 7. Hot H_2S and COS traps, tar scrubber, ammonia scrubber, and guard beds

Figure 8. Rear view; compressor, mass flow controller panel, power panel, scrubber water pumps

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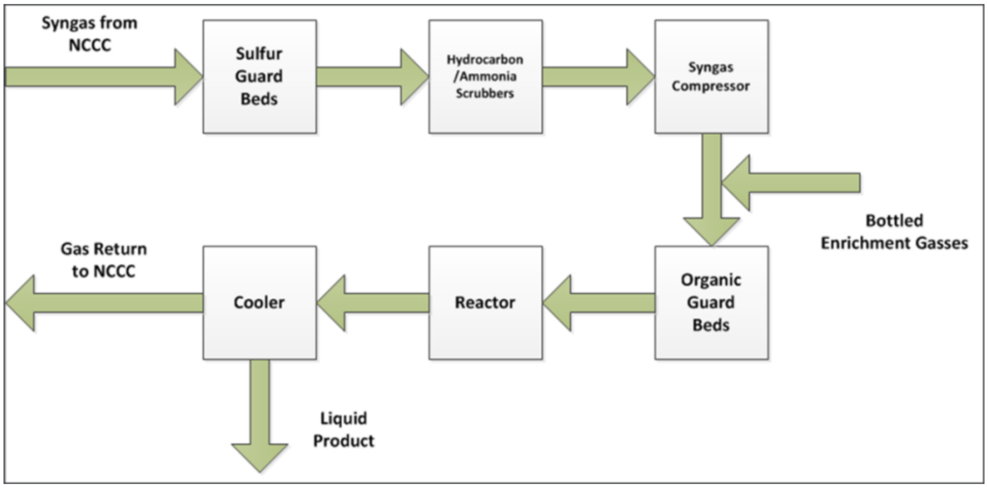

Figure 9. Schematic of SR-CBTL test rig installed at NCCC

This was done to increase its H_2/CO ratio to 2 and enrich it to simulate an oxygen-blown gasifier. The mixed gas (gasifier syngas and bottled syngas) was then sent to a series of guard beds for final polishing. These guard beds are designed to remove final traces of hydrocarbons, ammonia, sulfur and carbonyls. It then entered the 2 inch diameter fixed-bed FT reactor (with a cooling jacket) with Intramicron's MFEC catalyst packing and a water-based thermo-syphon heat removal system. Two FT reactors were built to have one as spare as shown in Figure 10.

Figure 10. Jacketed 2 inch diameter FT reactors with six position thermowell

The ability to supply synthetically blended H_2 and CO or pure H_2 serves several purposes, allowing for: (1) adjustment of the H_2-CO ratio to simulate a shift reactor; (2) increasing the H_2 and CO partial pressure, and thereby reducing CO2 and N2 partial pressures to make the syngas more representative of a commercial operation (CO_2 will be captured prior to FTS in a commercial embodiment) and suitable for FTS; (3) startup of the FTS reactor without the gasifier being in operation; (4) FTS to continue during a planned run even if the gasifier has to be shut down for safety reasons; (5) reduction/activation of the catalyst in-situ.

The combined gas also contained some nitrogen, methane and CO_2. The anticipated total concentration levels of these inert gases are 20 to 40 volume %. The clean syngas, combined with H_2 and CO to achieve a H_2/CO mol ratio of 2, had the nominal composition shown in the right hand column of Table 3. This table also shows the percent contribution of the syngas feed to the FT reactor from the NCCC gasifier and from bottles.

Table 3. Nominal Composition of the Syngas Feed to the FT Reactor after Blending

	Vol %			
	Air Blown Raw Syngas	From NCCC	From Bottles	Total
H_2O	7.60%	0.0%	0.0%	0.0%
CO	9.0%	4.2%	17.3%	21.5%
H_2	6.80%	3.2%	39.8%	43.0%
CO_2	8.30%	3.8%	0.0%	3.8%
CH_4	1.10%	0.5%	0.0%	0.5%
N_2	67.20%	31.1%	0.0%	31.1%
Total	100.00%	42.82%	57.18%	100.00%

The fixed-bed FT reactor was a vertical, down-flow, 316 stainless steel pipe with an internal diameter of 2 inches. Inert material was placed on top of the catalyst bed to provide distribution and preheat to the incoming syngas. Pre-reduced and passivated Chevron catalyst was packed in the reactor using Intramicron's microfiber-entrapped catalyst (MFEC) packing to facilitate rapid radial and axial heat transfer during reaction. The packed catalyst section contained 270 g of catalyst. Some inert material was also placed downstream of the catalyst.

FT Run

The run began with re-reduction and activation of the catalyst in-situ followed by slow increase of temperature and pressure to the desired operating conditions. The reaction heat was transferred rapidly to the reactor wall and then removed from the walls by boiling circulating water in the jacket produced by the thermo-syphon system. Once the catalyst reached steady state using bottled syngas, a portion of the bottled syngas was replaced by gasifier syngas. Gasifier syngas using coal was used first followed by gasifier syngas using coal + biomass, and finally the baseline conditions with bottled syngas were rerun to complete the test.

The FT reaction temperatures for the catalyst were in the 200-240^{o}C range and pressures tested were in the 190-280 psig range. The startup heat to the water in the jacket and serially to the catalyst was provided by surrounding heater cables with programmable temperature controllers. The thermo-siphon system not only prevented run away reaction, but also provided highly efficient heat removal for the FTS reaction and maintained the temperature near the desired value based on the cable heater setting. The high heat transfer coefficient due to vigorously boiling water in the top third section of the jacket extracted the maximum heat where the CO concentration was highest and maximum reaction occurred.

After the FT reactor, the FT tail gas went through a warm/hot trap to condense the relatively heavier hydrocarbons and then the tail gas was cooled to condense the water and hydrocarbon liquids. The two samples were then mixed after collection for mass balance purposes and for capillary gas chromatography (GC) analysis. A sample of both the inlet gas to the FT reactor and the gas leaving the liquid condenser was analyzed periodically using an on-line GC that measures H_2, CO, CO_2, CH_4, N_2 and C_2-C_5 hydrocarbons. The tail gas was then sent to the syngas return line.

The N_2 in the syngas feed and the FT tail gas was used as an internal standard in the GC analysis to facilitate conversion, selectivity and mass balance calculations. Composite water and oil samples collected periodically were weighed to check mass balance and shipped to Southern Research Labs for separation, preparation, and complete characterization to determine the hydrocarbon yield and distribution, and the oxygenated compounds in the water.

Feed and Product Analyses

Ground PRB coal and ground hardwood pellets (from American Wood Fibers) were used as the coal and biomass for the testing. Samples of the feed coal and biomass were subjected to proximate and ultimate analyses. The collected liquid samples naturally separated into an organic layer and water layer. Both were analyzed using capillary GC and capillary GC/MS. The hydrocarbon samples were also characterized using an Anton Paar Stabinger SVM 3000 viscometer for viscosity and density.

Results and Discussion

Following design, fabrication, and initial shakedown, the SR-CBTL test rig has been operated during two pre-scheduled gasifier runs in April and October of 2014. The April run demonstrated the required catalyst productivity but was terminated prematurely due to a heater failure. Valuable lessons that were learned from the April run resulted in the required Test Rig modifications (including an upgraded tar removal system for the gas sampling train, modified reactor heating system, and a more efficient product condenser) that allowed a successful slip stream run in October 2014.

The anticipated results from running the Chevron cobalt-zeolite hybrid catalyst included high catalyst productivity >0.7 g /(g catalyst)/h, a liquid hydrocarbon product distribution as shown in Figure 11 with carbon number peak at C9-C10, and production of clear liquids as shown in Figure 12 [Kibby et al. 2011].

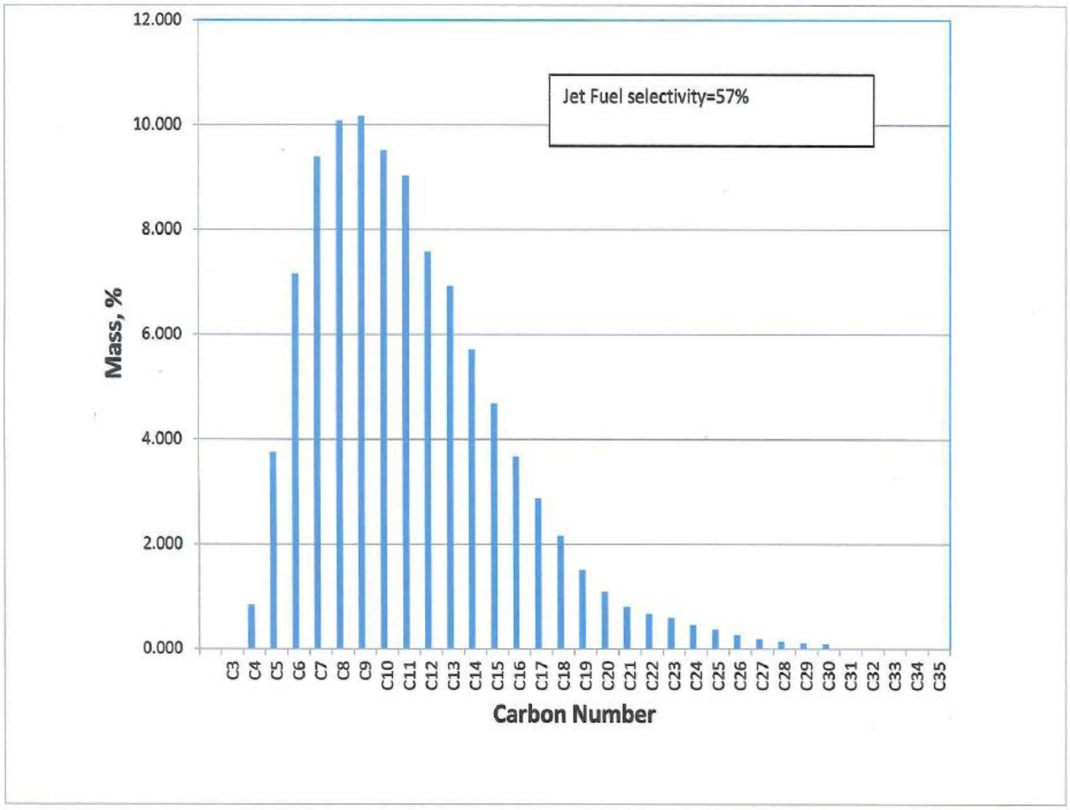

Figure 11. Typical liquid product distribution produced by Chevron catalyst with a peak at about C9.

Figure 12. Solid wax-free clear hydrocarbon liquids produced by Chevron catalyst

April 2014 Run

The first SRI-CBTL test campaign including final pressure testing, final system commissioning, limited bottled gas Fischer-Tropsch (FT) testing, and raw syngas cleanup testing has been carried out during April 5-19, 2014. The following successes were achieved during the run.

- Learned to safely operate the SRI-CBTL unit at required pressures and temperatures with simulated syngas (through FT catalyst reactor)and actual syngas (on hot sulfur removal and clean-up side)
- Successfully activated the Chevron cobalt Fischer-Tropsch catalyst using pure hydrogen
- Operated the raw syngas side of the unit for over 60 hours using bottled syngas
- Maintained H_2 to CO ratio of 1.95 to 2.01 during the bottled gas testing
- Demonstrated high catalyst hydrocarbon productivity of 0.65 to 0.75 g (as carbon) / g catalyst/h at 225^{o}C with 34 % H_2, 17 % CO and 49 % N_2.
- Demonstrated the production of >>2 L/day of hydrocarbon liquids from the SRI-CBTL unit.
- Demonstrated successful operation of pump-less thermal siphon heat removal system. Efficient heat removal and nearly isothermal condition was achieved in a 2 inch fixed-bed reactor.
- Demonstrated successful shutdown and recovery from shutdown during a hydrogen leak at the NCCC hydrogen supply tank.
- Successfully ran raw syngas at inlet pressure (175-190 psig) and temperature (450-600^{o}F) for over 24 hours.
- Verified syngas compressor operation
- Collected liquids were analyzed by GC/GC-MS. Since the operating temperature during collection of these liquids was lower than the design conditions, as expected, the liquids peaked at C15 hydrocarbon as opposed to a desired peak at C11.

A number of operational issues arose as bottled gas testing progressed including a hydrogen leak from the NCCC supply side causing shut down for a day. A major issue was a leaking pressure relief valve (even though the valve was designed to withstand much higher pressure and temperature than it was exposed to) on the steam drum for the thermos syphon system. Pressure relief lines had to be increased in diameter a couple of times as requested by NCCC to eliminate potential relief valve chattering. Following the restart after the hydrogen leak, progress was continued to attempt to reach the reaction design conditions of 280 psig and 245^{o}C adhering to the activation procedure specified by Chevron. At about 60 hours of operation however as the temperature of 230-235^{o}C was reached, the heater on the reactor failed and to conserve project resources, a decision was made to stop the run at this point.

Based on this experience, a need for the following modifications to the test-rig was identified and implemented. The reactor heating system needed to be fault tolerant with excess heating capacity. A reactor heating system based on 8 heating zones with excess heating capacity was designed and installed for the October run. The product collection system was significantly improved. A larger high temperature product collection tank was installed, and a double pipe coiled condenser was installed for efficient light hydrocarbon product collection. A more efficient heavy hydrocarbon/tar cooling/condensation/collection system was designed and installed. The process water sprayed in the tar scrubber was increased in flow and the water was chilled to lower temperatures prior to scrubbing using a larger cooler. Two larger tar solid filters were installed in parallel.

October 2014 Run

During the October 2014 Run, the slip stream test at NCCC was carried out with bottled syngas, coal-derived syngas and coal/biomass derived syngas in the following sequence: bottled simulated syngas for approximately 5 days following catalyst activation, Powder River basin (PRB) coal derived syngas augmented with bottled gas for approximately 3 days, and 80 % PRB coal and 20% woody biomass-derived syngas augmented with bottled gas for approximately 3 days, and finally bottled simulated syngas again for approximately 1 day to evaluate catalyst deactivation, if any.

The biomass used was ground hardwood pellets from American Wood Fiber. The ultimate and proximate analyses of the coal and wood are presented in Tables 4 to 6. The biomass had significantly higher volatile content (due to higher oxygen levels) and lower ash content than coal. The total carbon, hydrogen and nitrogen levels of the two fuels wee similar. The moisture content of the coal was much higher than the pelleted biomass. The BTU contents of the two fuels as fed are similar and around 8000 BTU/lb. The dry basis syngas slip-stream compositions of the run with coal and the run with coal + biomass are shown in Tables 7. The mixed gas compositions (bottled gas + syngas) for coal only and coal + biomass are shown in Tables 8 and 9, respectively.

Table 4: Ultimate analysis of feed coal and feed biomass

	Coal	Biomass
Carbon	55.7	47.2
Hydrogen	5.4	5.8
Nitrogen	1.6	1.3
Oxygen, Ash, Sulfur, etc*	37.4	45.7

* by difference

Table 5: Proximate analysis of feed coal

	1/5 001	1/5 002	1/6 001	1/6 002	1/8 001	Average
Moisture	19.1%	20.2%	19.2%	11.3%	19.4%	17.8%
Volatile Carbon	36.2%	28.3%	29.1%	35.6%	32.6%	32.4%
Fixed Carbon	38.3%	45.2%	45.4%	46.1%	42.4%	43.5%
Ash	6.4%	6.3%	6.3%	7.0%	5.6%	6.3%

Table 6: Proximate analysis of feed biomass

	1/6 001	1/6 002	1/8 001	Average
Moisture	7.1%	7.2%	7.0%	7.1%
Volatile Carbon	71.4%	70.5%	74.3%	72.1%
Fixed Carbon	20.7%	21.5%	18.1%	20.1%
Ash	0.8%	0.7%	0.5%	0.7%

Table 7. Syngas slipstream composition (dry basis)

	Coal	Coal/Biomass
N2	70.1%	71.4%
CO	10.6%	9.5%
CO2	9.7%	10.2%
CH4	1.1%	1.3%
C2+	0.0%	0.0%
H2	7.9%	7.2%
H20	0.0%	0.0%
H2S	0.038%	0.028%
Total	100.0%	100.0%

Table 8. Measured and Calculated Coal Syngas Composition Fed to FT Reactor After Mixing with Bottled Gas

Syngas from coal only feed	Measured NCCC Syngas Comp	Calculated Flow From NCCC (SLPM)	Measured Flow From Mixing Panel (SLPM)	Total Flow to Reactor (SLPM)	Measured GC Measurement	Expected Syngas Composition
H2	7.93%	1.8	22.5	24.30	43.48%	42.63%
N2	70.11%	16.0	1.0	17.00	29.88%	29.82%
CO	10.56%	2.4	10.7	13.10	21.29%	22.98%
CH4	1.15%	0.3		0.26	0.43%	0.46%
CO2	9.75%	2.2		2.23	5.11%	3.90%
Total	99.49%	22.8	34.2	57.00	100.19%	100.00%

Table 9. Measured and Calculated Coal + Biomass Syngas Composition Fed to FT Reactor After Mixing with Bottled gas

Syngas from blended coal/biomass feed	Measured NCCC Syngas Comp	Calculated Flow From NCCC (SLPM)	Measured Flow From Mixing Panel (SLPM)	Total Flow to Reactor (SLPM)	Measured GC Measurement	Expected Syngas Composition
H2	7.17%	1.6	22.1	23.68	42.99%	41.59%
N2	71.41%	15.8	1.0	16.82	29.73%	29.54%
CO	9.45%	2.1	11.7	13.79	21.45%	24.21%
CH4	1.27%	0.3		0.28	0.48%	0.49%
CO2	10.22%	2.3		2.26	6.01%	3.97%
Total	99.52%	22.2	34.8	56.94	100.66%	100.00%

For data quality control, the gas compositions were measured as well as calculated on the basis of flows and these were found to be in reasonably good agreement as shown in Tables 8 and 9.

Following the run, test data was reduced and analyzed, and liquid products were characterized to evaluate differences, if any, between liquid from bottled simulated syngas, coal, and coal + biomass. The key results are presented below and a complete set of results for the hydrocarbon liquids and aqueous samples characterizations is presented in Appendix. The run demonstrated the following:

- A smoothly operating Test Rig with seamless transitions from bottled gas to coal to coal-biomass and back to bottled gases; efficient removal of solid tar using the gas cleaning system allowing plug-free long-term operation;

- Syngas clean-up system cleaned the feed gases to ultra-low impurity levels except, as discussed later, the slip of certain sulfur species that could not be captured efficiently and accumulated on the catalyst
- The production of >>2 L/day of hydrocarbon liquids from the CBTL Test Rig;
- High hydrocarbon productivity of >4 times conventional catalysts
- Preliminary observations did not show significant differences between bottled gas feed, coal syngas feed and coal-biomass syngas feed; seamless switch
- Efficient heat removal and management demonstrated in the 2 inch id fixed bed reactor
- Liquid product was nearly wax free
- High Productivity demonstrated (65 % H2+CO, 35 % inert)
  - 195 psig: ~0.54 g HC/g catalyst/h
  - 280 psig: ~0.72 g HC/g catalyst/h
- Solid wax free liquid production, low methane selectivity (<16.5 %), and >74 % selectivity to C_5 + liquid hydrocarbons; No selectivity change over the course of the test operated for approximately 350 hours
- A small amount of catalyst deactivation that was potentially linked to unknown sulfur species causing sulfur accumulation on the catalyst as described below

<u>Key Results from October Test</u>

A complete set of results for the hydrocarbon liquids and aqueous samples characterizations is presented in Appendix. Results summarizing the process conditions, conversion and selectivities are provided in Figure 13. As indicated earlier, bottled gases were run first at 280 psig, followed by coal based syngas at a somewhat lower pressure of 190 psig (to avoid the complication of using the compressor), followed by coal + biomass-based syngas at the same pressure, and finally followed by return to bottled gas at 280 psig baseline conditions. The temperature was held constant during the test at 240°C. As can be seen from Figure 13, the selectivities remain unchanged after exposure to slip stream syngas, and there appears to be no difference in productivity and selectivity between the use of coal syngas and coal + biomass syngas. Increased pressure as expected increases selectivity slightly to C5 + and reduces the corresponding amount to C1 to C4.

The small catalyst deactivation (indicated by gradually lower conversion) that was observed over the duration of the test was potentially linked to traces of sulfur in the syngas accumulating on the catalyst. Sulfur levels of up to ~150 ppmw with levels decreasing with higher downstream bed position, were found on the used catalyst as shown in Figure 14. Since sulfur in the fresh catalyst was below detection limit, the measured level of sulfur of ~60-164 ppmw is quite significant. Furthermore, since a hot polishing bed followed by a low temperature polishing bed was used for efficiently removing H_2S and COS to ppb levels from syngas, it is possible that sulfur found on the catalyst potentially came from other sulfur species such as

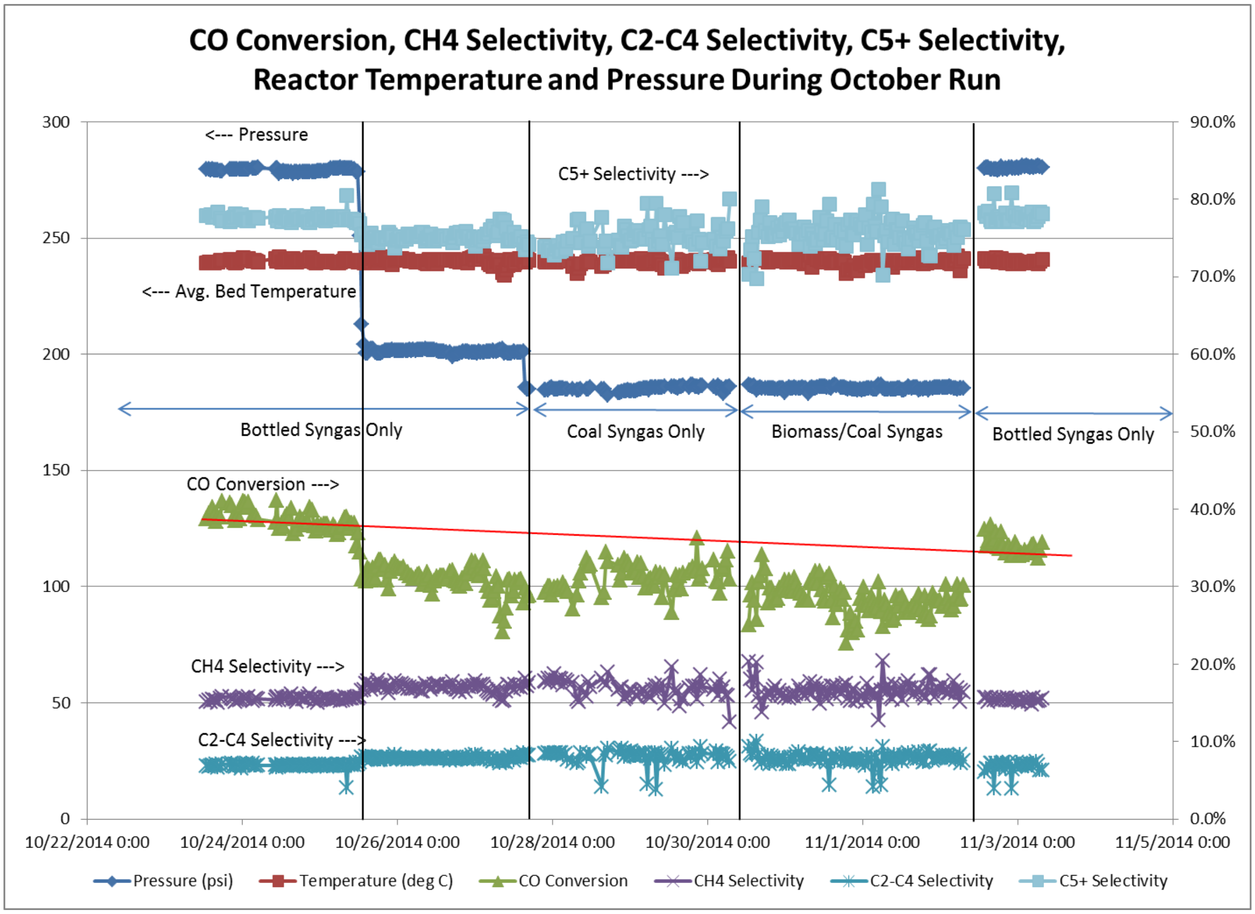

Figure 13. FT conversion and selectivity results during second slip stream test

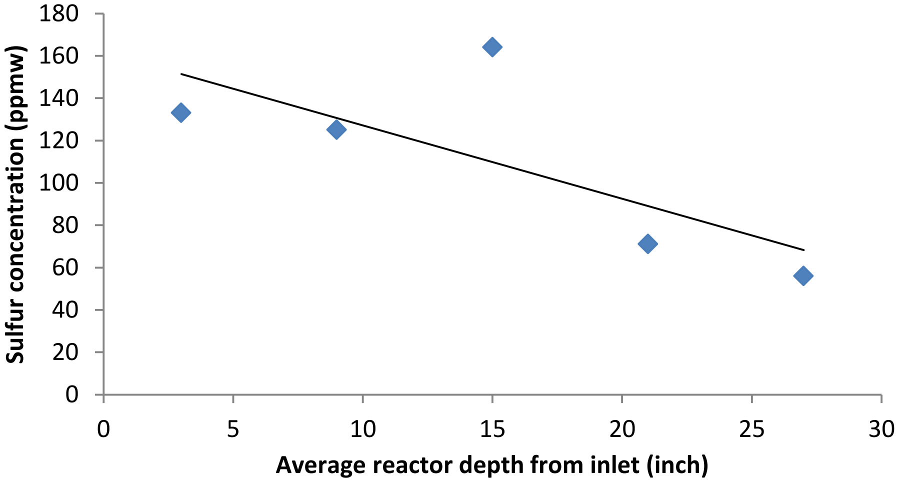

Figure 14. Sulfur accumulation on catalyst during October slip stream test

mercaptans, sulfides and/or thiophenes. However, breakthrough of H_2S and COS from the guard beds into the FT reactor cannot be ruled out from the results obtained. Considering that sulfur is a strong poison to cobalt catalysts, the Chevron cobalt-zeolite hybrid catalyst exhibited significant resistance to sulfur.

The liquid samples collected were separated into an organic fraction and an aqueous fraction. Results of capillary GC analysis of the organic fractions from the bottled gas run before and after the slip stream syngas runs are compared in Figures 15.

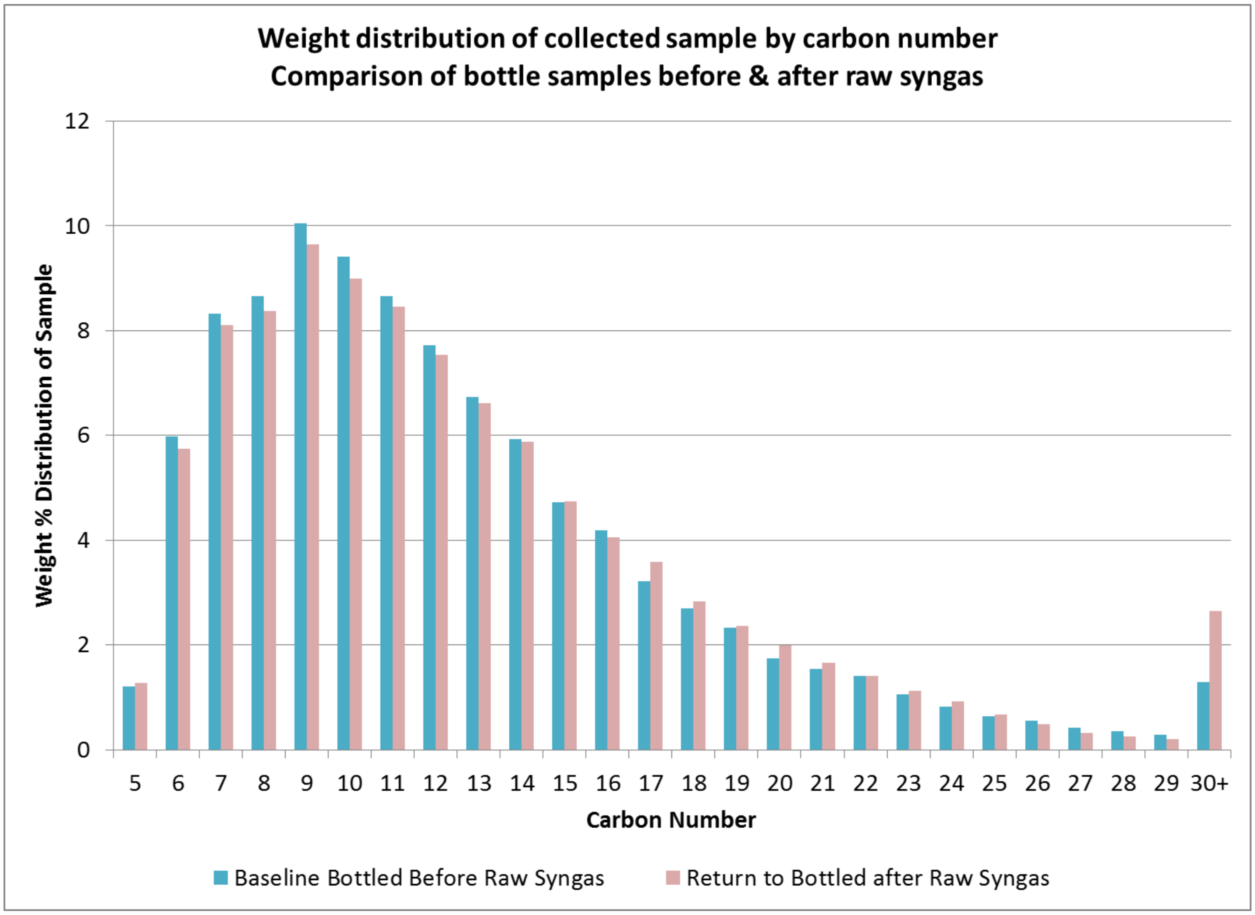

Figure 15. FT Liquid product with bottled syngas before and after gasifier syngas exposure

As can be seen, there is not a significant difference between the two, further corroborating that the catalyst selectivity did not change. There was more than expected heavier hydrocarbons beyond C20 produced. This was attributed to lower catalyst bed temperature than desired in the lower section of the reactor. Unfortunately, in the current set up of the multi-junction thermocouple, the upper temperatures and bed exit temperature were measured but the temperatures in the lower half of the catalyst bed were not measured. It was found that there was insufficient heat in the water down-comer from the steam drum to increase the water temperature to the reaction temperature of 235 to 240^{o}C. Using COMSOL Multiphysics software, an axial temperature distribution in the lower section of the bed was estimated as shown in Figure 16.

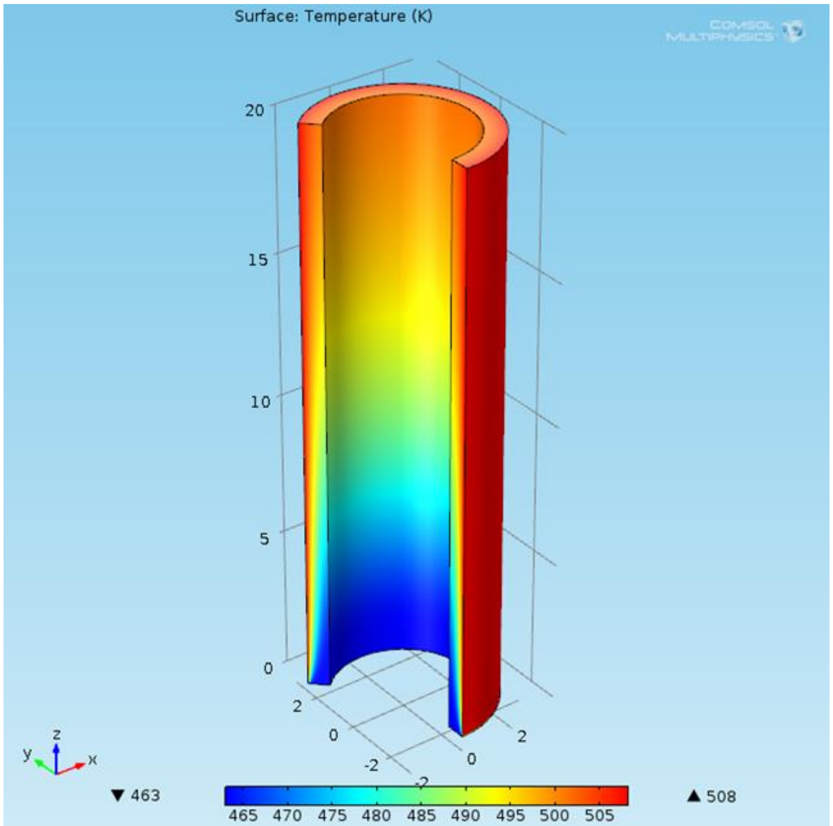

Figure 16. Estimated axial temperature distribution in lower half of reactor (K)

As seen, the catalyst bed was lower in the lower sections, and did not reach 235^{o}C (508 K) until about 9 inches into the catalyst bed from the bottom. The lower temperature caused the formation of heavier compounds in the lower section of the bed as seen in the product distribution, but even so the liquid product produced was solids free as shown in Figure 17. Also, if the temperatures of 235 to 240 C were reached throughout the bed, the hydrocarbon productivity would have been even greater than the respectable number of >0.7 g/g catalyst /hr that was achieved.

The liquid product distributions of the run with coal syngas and with coal + biomass syngas are compared in Figure 18. As seen, there appears to be no effect of biomass addition to coal on FT liquid products made. But, comparing the results in Figures 15 and 18, it is seen that higher pressure, as expected, shifted the product distribution towards heavier hydrocarbons. The hydrocarbon distribution peak is at C9 which is in agreement with Chevron’s results from lab scale studies (Figure 11).

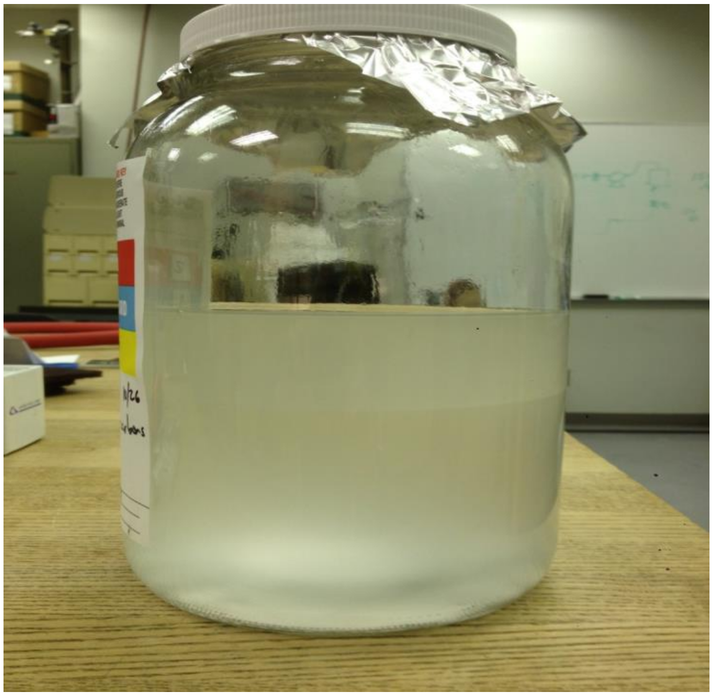

Figure 17. Liquid product showing absence of solid wax

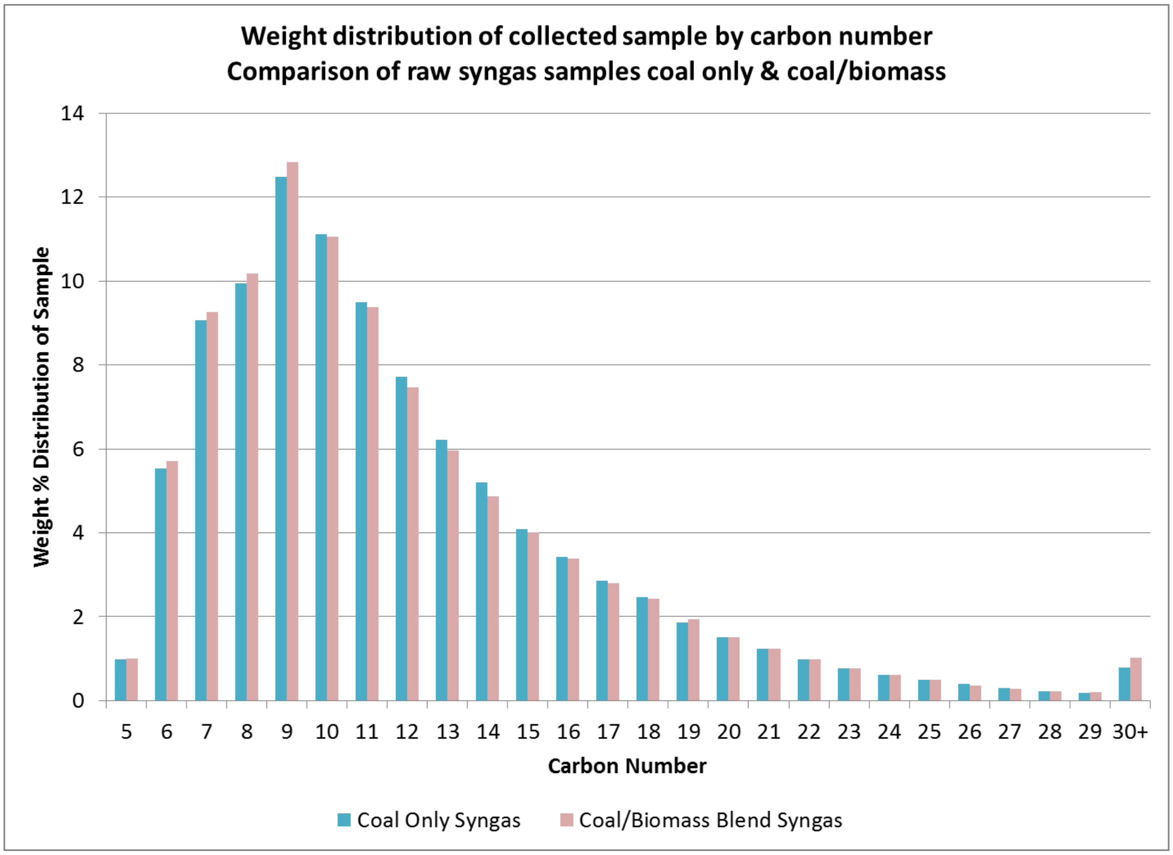

Figure 18. Comparison of FT liquid products from coal and coal/biomass syngas

The measured viscosity and density of the FT liquids during the various operating regimes are compared to jet fuel and diesel standards in Table 10. As expected, the densities are lower for the FT products due to the absence of aromatic compounds. Also, the viscosities are a bit lower possibly due to the absence of aromatic compounds and presence of naphtha range hydrocabons that are typically present at low levels in jet fuel and diesel.

Table 10. Viscosity and Density of FT Liquids Compared to Diesel and Jet Fuel Standard

	Kinematic Viscosity (mm^2/s)	Density (kg/m^3)
Diesel 1D Standard[1]	1.3-2.9	
Jet Fuel Standard[2]	< 8	775-840
Bottled Syngas Liquid Sample[1]*	1.25	732
Coal Syngas Liquid Sample[1]*	1.01	728
Biomass/Coal Syngas Liquid Sample[1]*	1.00	728
Bottled Syngas Liquid Sample[1]*	1.27	732

1: Measured at 40°C; 2: Viscosity measured at 20°C, Density at 15°C; * Did not fractionate sample prior to measurements.

In addition to characterizing the organic product, the aqueous products were also analyzed by capillary GC. A typical result for the aqueous sample is shown in Table 11. The results indicate the product to be mostly water (~97 wt %) and balance oxygenated compounds, primarily methanol (~2 wt%) and ethanol (0.7 wt%). Total organic carbon as measured using the HACH test for the aqueous fraction of the final sample collected during the run indicated that about 1 % of the carbon in the feed ended up in the aqueous phase

Table 11. Typical Composition of Aqueous FT Product

Trial #	20141102
Trial Name	CBTL Aqueous Solution
Methanol	1.98%
Ethanol	0.73%
2-Propanol	0.06%
Methyl Acetate	0.02%
1-Propanol	0.21%
Ethyl Acetate	0.00%
2-Methyl-1-Propanol	0.01%
1-Butanol	0.09%
Ethyl Propionate	0.01%
Propyl Acetate	0.00%
2-Methyl-1-Butanol	0.01%
1-Pentanol	0.05%
Water %	96.73%
2-Butanol	0.02%
3-Methyl-1Butanol	0.00%
Butyl Acetate	0.00%
Hexanol	0.03%
new compounds	0.05%
Total Mass %	99.95%

Preliminary TEA and LCA

A preliminary TEA and LCA was carried out to determine the cost reduction potential for selective FT and greenhouse gas (GHG) emission reduction potential for using 20 % biomass with coal. The process design reference used for the CTL baseline was 23,000 tpd Shell gasifier case with CO_2 sequestration in the report done by the National Energy Technology Laboratory; "The Cost and Performance Baseline for Fossil Energy Power Plants, Volume 4: Coal-to-Liquids via Fischer-Tropsch Synthesis". Three gasification cases of equal plant size corresponding to 23,000 tpd coal were considered:

- CTL baseline [DOE/NETL, 2014]
- CTL with selective FT
- CBTL (80 % coal, 20 % biomass) with selective FT

The equipment considered is shown in Table 12. For preliminary cost comparison of the three cases, all equipment costs were assumed to be the same except for the FT synthesis, hydrocarbon recovery, and upgrading.

Table 12. Case Study Equipment Matrix

	CTL Selective FT	CBTL Selective FT	CTL Baseline Case
Coal Handling	✓	✓	✓
Biomass Handling		✓	
Air Separation Unit	✓	✓	✓
Water system	✓	✓	✓
TRIG™ Gasifier	✓	✓	✓
Particulate Filtration	✓	✓	✓
Gas Cooler	✓	✓	✓
Partial Water-Gas Shift reactors	✓	✓	
Mercury Removal	✓	✓	✓
Rectisol Unit	✓	✓	✓
Claus Plant	✓	✓	✓
Slurry Bed Reactor			✓
Fixed Bed Reactor	✓	✓	
Hydrocarbon Recovery	✓	✓	✓
CO_2 capture	✓	✓	✓
Product Upgrading			✓
Hydrogen Recovery			✓
CO2 compression and sequestration	✓	✓	✓
Combined Cycle Power Generation	✓	✓	✓

Furthermore for simplicity, it was assumed that all the plants made the same amount of liquid hydrocarbons. For the FT synthesis, since the selective FT catalyst was ~4-5 times more productive, the reactor was scaled down conservatively to ¼ the size, and the cost was reduced using the 6/10th rule for equipment size versus cost. According to this rule, the equipment cost is proportional to the size to the power 0.6. The hydrocarbon recovery section for the selective synthesis plants was assigned a cost which was ½ the cost of the hydrocarbon recovery section of the baseline plant. The upgrading section was eliminated for the selective synthesis plant. With these assumptions, the plant costs are shown in Table 13.

Table 13. Total Plant Costs ($ million; does not include land, financial and initial labor and inventory cost)

	CTL Selective FT	CBTL Selective FT	CTL Baseline
Slurry bed reactor			376.3
Fixed bed reactor	163.8	163.8	
Hydrocarbon recovery	69.6	69.6	139.2
Upgrading			102.5
Balance of Plant	4,656	4,656	4,656
Total	4,889	4,889	5,274

Thus, the total plant costs for the plants with the selective FT are approximately 7.3 % lower than the baseline CTL case with conventional FT. The cost of production of the FT liquids for the selective FT liquids was correspondingly lower by about 5.4 %. In the baseline plant, the capital cost of the FT reactor, hydrocarbon recovery, and upgrading sections represented only 11.7 % of the total cost of the plant, based on the data provided in the NETL report. The costs of these sections can be as much as 35 % of the total cost of the plant [Choi et al., 1996]. The cost savings using the selective FT will increase as the percent cost of these sections increase.

The life cycle analysis of the liquid fuels was calculated based on a "well-to-wheel" (WTW) basis. This means that all greenhouse gas emissions associated with the life-cycle of this product from feedstock extraction, to fuel production, and finally fuel combustion in an automobile are considered. All factors for each step of the process were taken from Argonne National Laboratory's "*Greenhouse Gas, Regulated Emissions, and Energy Use in Transportation Model"* (GREET), GREET 2014. The emission factors used from GREET are shown in Table 8.

The upstream factors from GREET only include the production of the fuel. In order to calculate the use of the fuel, the total carbon content of the fuel (i.e. biomass, fuel gas, etc) was converted to a CO_2 equivalent assuming 100% complete combustion. Biomass was assumed to be 100% biogenic, removing its entire carbon content from the atmosphere; therefore it's

$CO_{2equivalent}$ (CO_2e) is negative. The emissions were normalized based on the lower heating value (LHV) of 1 gigajoule (GJ) of finished fuel. The final net GHG emissions are presented in Table 15 and compared to a petroleum baseline.

Table 14. Emission factors from GREET model

Upstream Factors			
GREET Description	Factor Name	kg CO2e	per unit
Poplar Production for Ethanol Plant	Biomass	85.47	ton
Coal for Power Plants	Coal	122.19	ton
Mix: Natural Gas - Methanol	Methanol	537.56	ton
Downstream Factors			
GREET Description	Factor Name	kg CO2e	per unit
Gasoline Blendstock from Crude Oil (to Bulk Terminal & to Refueling Station)	Transport	23.79	ton

Table 15. Results of LCA

	Greenhouse Gas (WTW) Emissions per 1 GJ
Petroleum Baseline	Gasoline: 66 kg Diesel: 93 kg
CTL Baseline	126 kg
CTL Selective FT	126 kg
CBTL Selective FT	92 kg

Conclusions

Southern Research has developed a fully functional CBTL test-rig and installed it on a slip stream alongside a large pilot-scale gasifier at NCCC that is being scaled up for commercial operation at Kemper County, Mississippi. SR's test-rig can be utilized to test alternate FT catalysts and conditions to promote and assist CBTL scale up and commercialization.

SR's 2 inch diameter fixed-bed FT reactor system with Intramicron's MFEC packing and thermos-syphon heat removal system demonstrated excellent heat management capability. Also, seamless switch was achieved from bottle gas feed to coal syngas feed to coal + biomass syngas feed and back to bottled syngas feed. There appeared to be little effect of adding biomass at 20 % level to coal on the gasifier gas make, FT reaction, and FT products.

The test verified the expected Chevron catalyst results of high productivity (>0.7 g/g catalyst/h), solid wax-free product and high liquid product selectivity (75 % to C_5-C_{20}). Sulfur in the coal and/or coal+biomass syngas was the primary contaminant that was detected on the used catalyst and was potentially responsible for the slight deactivation. Even so, the catalyst exhibited significant resistance to potential sulfur poisoning.

Based on the TEA/LCA, the addition of biomass to coal has the potential of reducing the carbon foot print of CBTL compared to CTL and to bring it closer to the carbon foot print of petroleum-based fuel production processes. However, technical and logistic issues with biomass include biomass collection infrastructure, biomass availability radius, and co-feeding of coal with biomass. For a conventional FT plant with capital cost of 11.7 % for the FT and upgrading sections, there is a potential for about 7 % capital cost and 5 % product cost reduction due to the use of a high activity and selectivity catalyst and elimination of wax upgrading. Competition with petroleum-based liquids at current prices would require collective improvements and cost reductions not just in FT and upgrading but in all major CTL/CBTL plant unit operations.

Recommendations

It is recommended that the functional SRI skid-mounted system at NCCC be leveraged on other projects to conduct slip stream tests during future gasification campaigns. In particular, the catalyst bed temperatures should be monitored and controlled axially to allow full utilization at wax-free conversion conditions. Sulfur breakthrough from a series of guard beds capable of picking up H_2S and COS should be further investigated. Dual guard beds in parallel should be installed to allow uninterrupted long-term testing. Other forms of potential sulfur compounds such as mercaptans, sulfides and thiophenes should be evaluated in the syngas. Online analytical techniques should be developed to monitor their breakthrough. If they break through the guard beds, techniques should be developed to capture them prior to the FT reactor. Following the development and implementation of techniques to completely remove both inorganic and organic sulfur compounds in syngas, a long-term slip stream test (500-700 hours) needs to be conducted to verify catalyst performance and long-term stability, and to provide sufficient design, engineering, and operating data for scale up. To enable design of pilot and demonstration scale FT systems, models should be developed using the data obtained for larger diameter (up to 6 inch) fixed bed FT reactors with high liquid selectivity and activity FT catalyst and MFEC packing. Based on this model, a technology transfer package should be prepared to attract industry to participate in scale up and demonstration of the technology.

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ACRONYMS AND ABBREVIATIONS

ASF	Anderson-Schulz-Flory
CBTL	Coal-biomass to liquids
CTL	Coal to liquids
DOE	Department of Energy
FT	Fischer-Tropsch
FTS	Fischer-Tropsch synthesis
GHG	Greenhouse gas
GREET	Greenhouse gas, regulated emission, and energy use in transportation
LCA	Lifecycle assessment
LHV	Lower heating value
MFEC	Microfibrous entrapped catalyst
NCCC	National Carbon Capture Center
NETL	National Energy Technology Laboratory
PDAC	Pressure decoupled advanced coal
PLC	Programmable logic controller
PRB	Powder River basin
RFS	Renewable fuel standard
SC	Southern Company
SCU	Syngas conditioning unit
SR	Southern Research
TEA	Techno-economic analysis
TRIG	Transport integrated gasification
WTW	Well to wheel

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Appendix

Table A1: Summary of liquid sample data

Sample No.	Syngas Composition	Sample Length	Set Pres. (psi)	Set Temp. (°C)	Total Sample Weight (g)	Organic Layer (g)	Aqueous Layer(g)
CBTL102415-04	Bottles Only	4 hr	280	240	1,374	431	943
CBTL102615-08	Bottles Only	8 hr	200	240	1,963	479	1,472
CBTL102715-24	Bot. + Coal Gas	24 hr	185	240	5,692	1,351	4,331
CBTL102815-24	Bot. + Coal Gas	24 hr	185	240	5,514	1,212	4,302
CBTL103015-24	Bot. + Coal/Bio. Gas	24 hr	185	240	5,294	1,102	4,192
CBTL103115-24	Bot. + Coal/Bio. Gas	24 hr	185	240	4,677	861	3,808
CBTL110215-14	Bottles Only	14 hr	280	240	4,129	1,260	2,869

Table A2: Measured total organic carbon in aqueous layer of decanted sample

Sample No.	TOC Result (mg/L)
CBTL102415-04	10780
CBTL102615-08	10920
CBTL102715-24	10640
CBTL102815-24	11000
CBTL103015-24	10700
CBTL103115-24	10820
CBTL110215-14	11860

Table A3: Alcohol analysis of aqueous layer of decanted sample

	Methanol	Ethanol	1-Propanol	1-Butanol	Total Mass %
CBTL102415-04	1.60%	0.67%	0.16%	0.01%	2.44%
CBTL102615-08	1.60%	0.67%	0.16%	0.06%	2.49%
CBTL102715-24	1.52%	0.67%	0.17%	0.06%	2.41%
CBTL102815-24	1.57%	0.69%	0.17%	0.06%	2.50%
CBTL103015-24	1.57%	0.66%	0.17%	0.06%	2.45%
CBTL103115-24	1.64%	0.68%	0.17%	0.06%	2.56%
CBTL110215-14	1.72%	0.64%	0.16%	0.07%	2.60%

Table A4: Measured dynamic viscosity and density in organic fraction of decanted sample

Sample No.	Pressure (psi)	Temperature (°C)	Dynamic Viscosity (mPa*s)		Density (g/cm^3)	
			Ave	St. Dev.	Ave	St. Dev.
CBTL102415-04	280	240	0.912	0.010	0.732	0.000
CBTL102615-08	200	240	0.772	0.000	0.731	0.000
CBTL102715-24	185	240				
CBTL102815-24	185	240	0.721	0.018	0.728	0.000
CBTL103015-24	185	240	0.725	0.012	0.728	0.000
CBTL103115-24	185	240				
CBTL110215-14	280	240	0.932	0.003	0.732	0.000

Table A5: Simulated distillation of organic fraction of decanted sample

Sample No.	CBTL102415-04	CBTL102615-08	CBTL102715-24	CBTL102815-24	CBTL103015-24	CBTL103115-24	CBTL110215-14
Syngas Composition	Bottles Only	Bottles Only	Bot. + Coal Gas	Bot. + Coal Gas	Bot. + Coal/Bio. Gas	Bot. + Coal/Bio. Gas	Bottles Only
Set Pressure (psi)	280	200	185	185	185	185	280
Set Temp. (°C)	240	240	240	240	240	240	240
Hydrocarbon Carbon Number							
C4	0.32%	0.12%	0.34%	0.12%	0.24%	0.26%	0.33%
C5	2.02%	1.12%	1.79%	0.81%	1.44%	1.43%	1.79%
C6	5.30%	4.25%	4.92%	2.94%	4.39%	4.21%	4.82%
C7	8.26%	8.25%	8.55%	6.27%	8.14%	7.71%	7.67%
C8	7.86%	8.92%	9.02%	7.61%	8.94%	8.35%	7.43%
C9	10.32%	11.77%	11.77%	10.53%	11.69%	11.07%	9.78%
C10	9.69%	10.91%	10.94%	10.55%	10.92%	10.42%	9.25%
C11	8.83%	9.48%	9.48%	9.70%	9.38%	8.88%	8.49%
C12	7.80%	7.84%	7.77%	8.35%	7.63%	7.16%	7.57%
C13	6.74%	6.42%	6.30%	7.07%	6.19%	5.90%	6.64%
C14	5.70%	5.26%	5.11%	5.93%	5.08%	5.04%	5.72%
C15	4.74%	4.34%	4.18%	4.99%	4.25%	4.40%	4.97%
C16	3.94%	3.62%	3.47%	4.24%	3.61%	3.90%	4.00%
C17	3.26%	3.01%	2.86%	3.57%	3.04%	3.41%	3.45%
C18	2.81%	2.74%	2.34%	3.09%	2.54%	2.92%	3.02%
C19	2.25%	1.78%	1.95%	2.36%	2.14%	2.51%	2.34%
C20	1.69%	1.61%	1.48%	1.94%	1.67%	2.00%	1.93%
C21	1.50%	1.31%	1.20%	1.58%	1.36%	1.63%	1.64%
C22	1.24%	1.06%	0.96%	1.28%	1.10%	1.32%	1.36%
C23	1.02%	0.87%	0.76%	1.04%	0.89%	1.07%	1.10%
C24	0.83%	0.72%	0.62%	0.84%	0.71%	0.86%	0.88%
C25+	0.74%	0.60%	0.52%	0.80%	0.64%	0.70%	0.76%

Figure A1: Simulated distillation chromatograph for sample CBTL102415-04

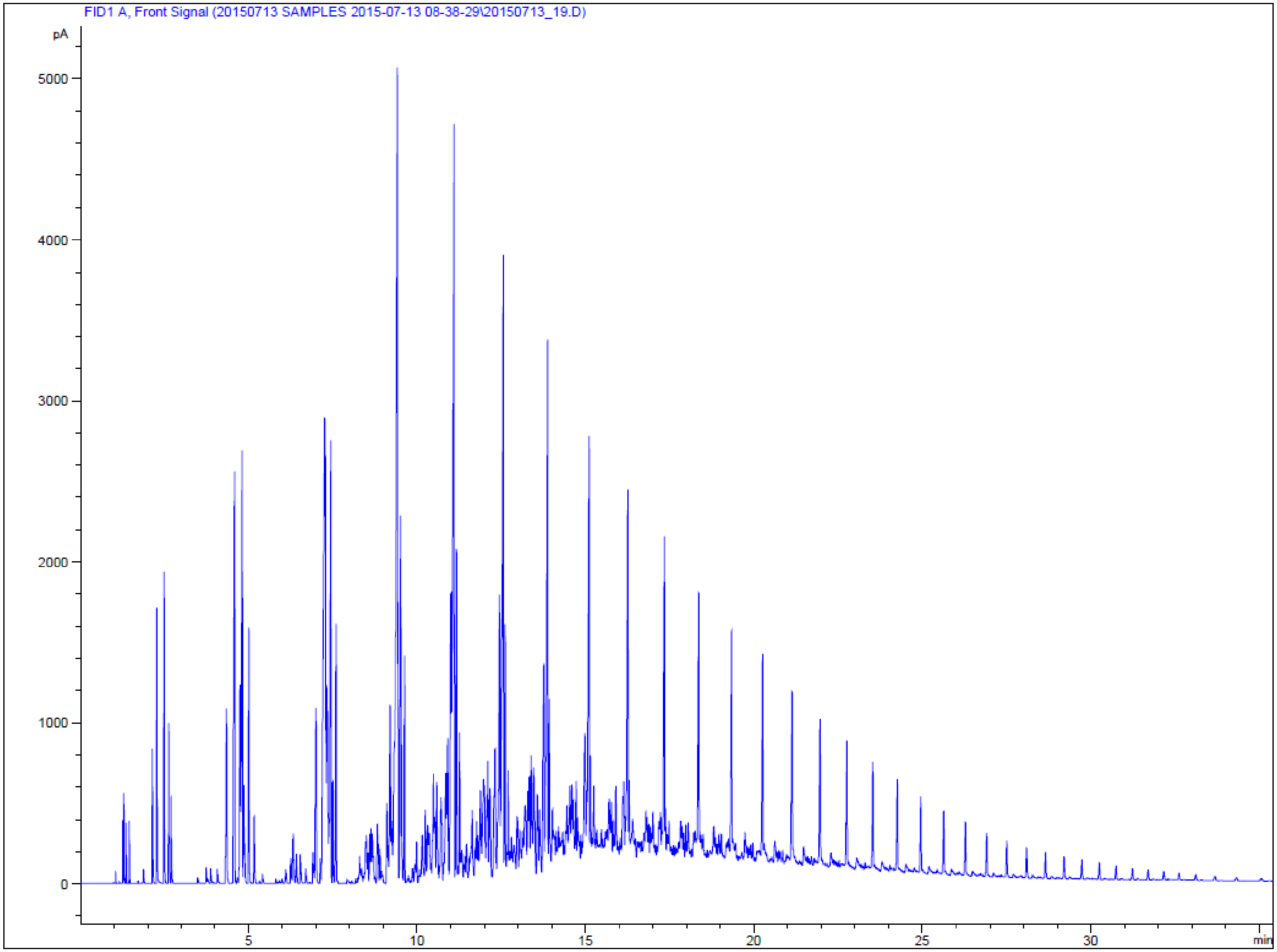

Figure A2: Simulated distillation chromatograph for sample CBTL102615-08

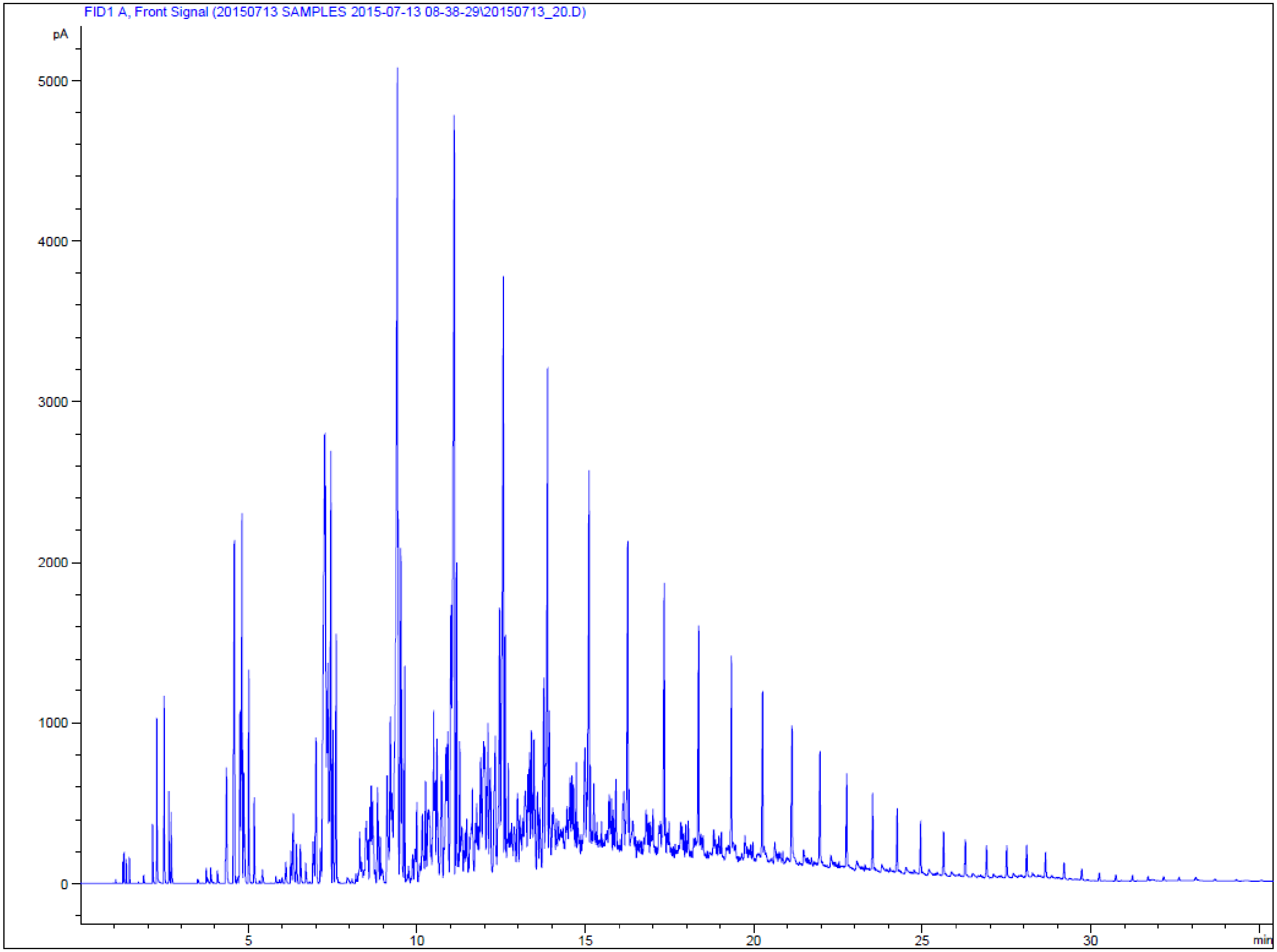

Figure A3: Simulated distillation chromatograph for sample CBTL102715-24

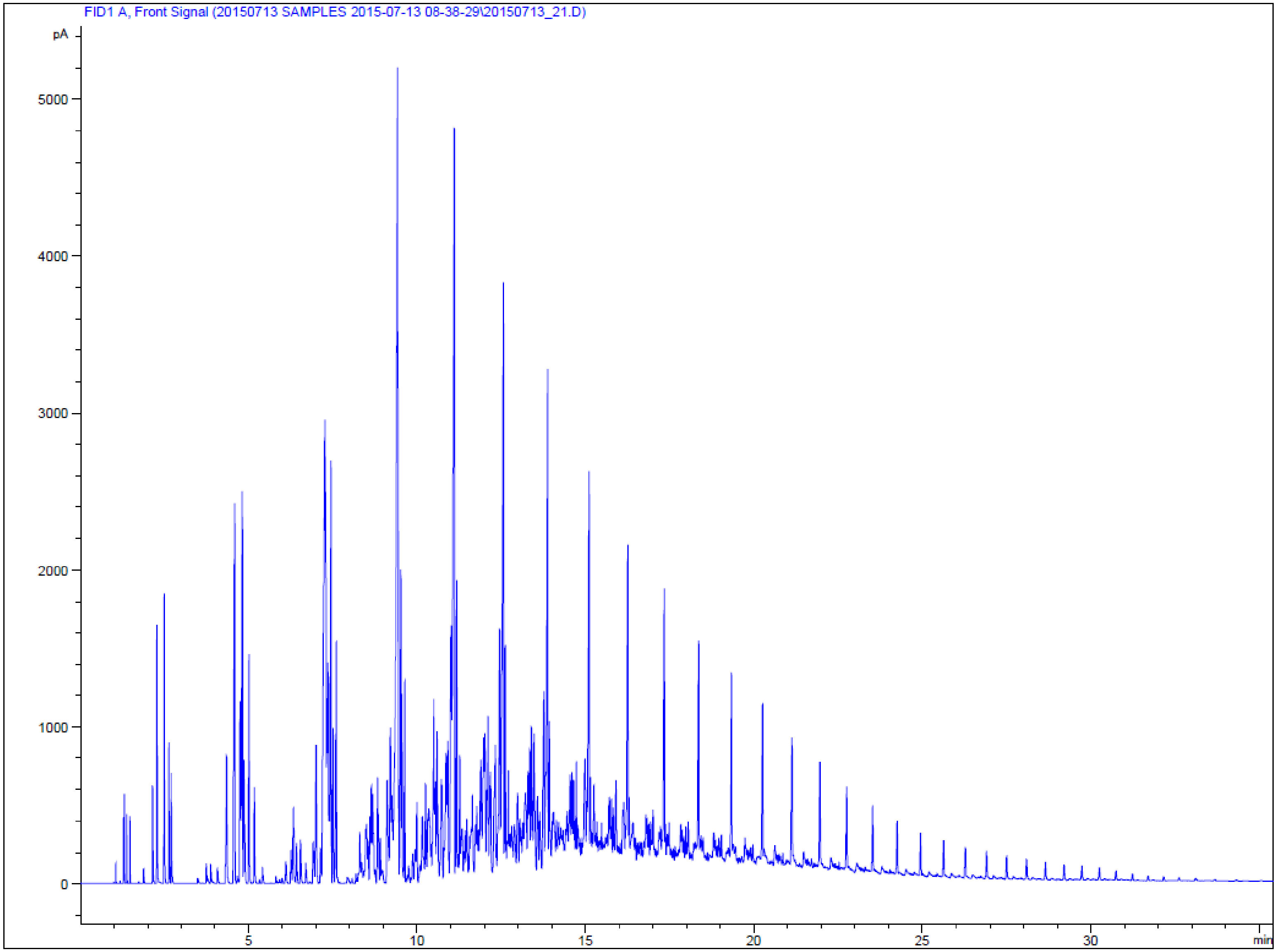

Figure A4: Simulated distillation chromatograph for sample CBTL102815-24

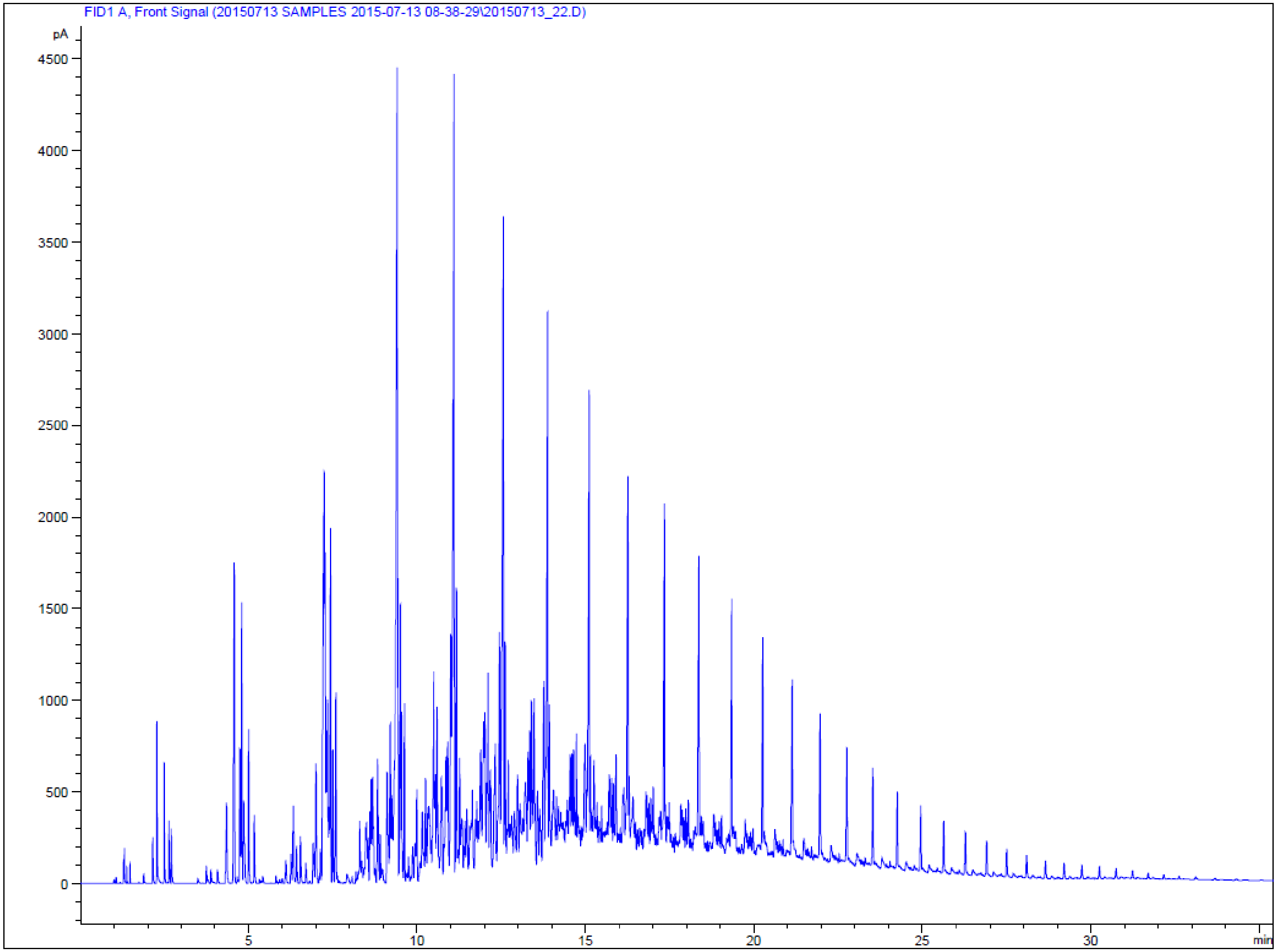

Figure A5: Simulated distillation chromatograph for sample CBTL103015-24

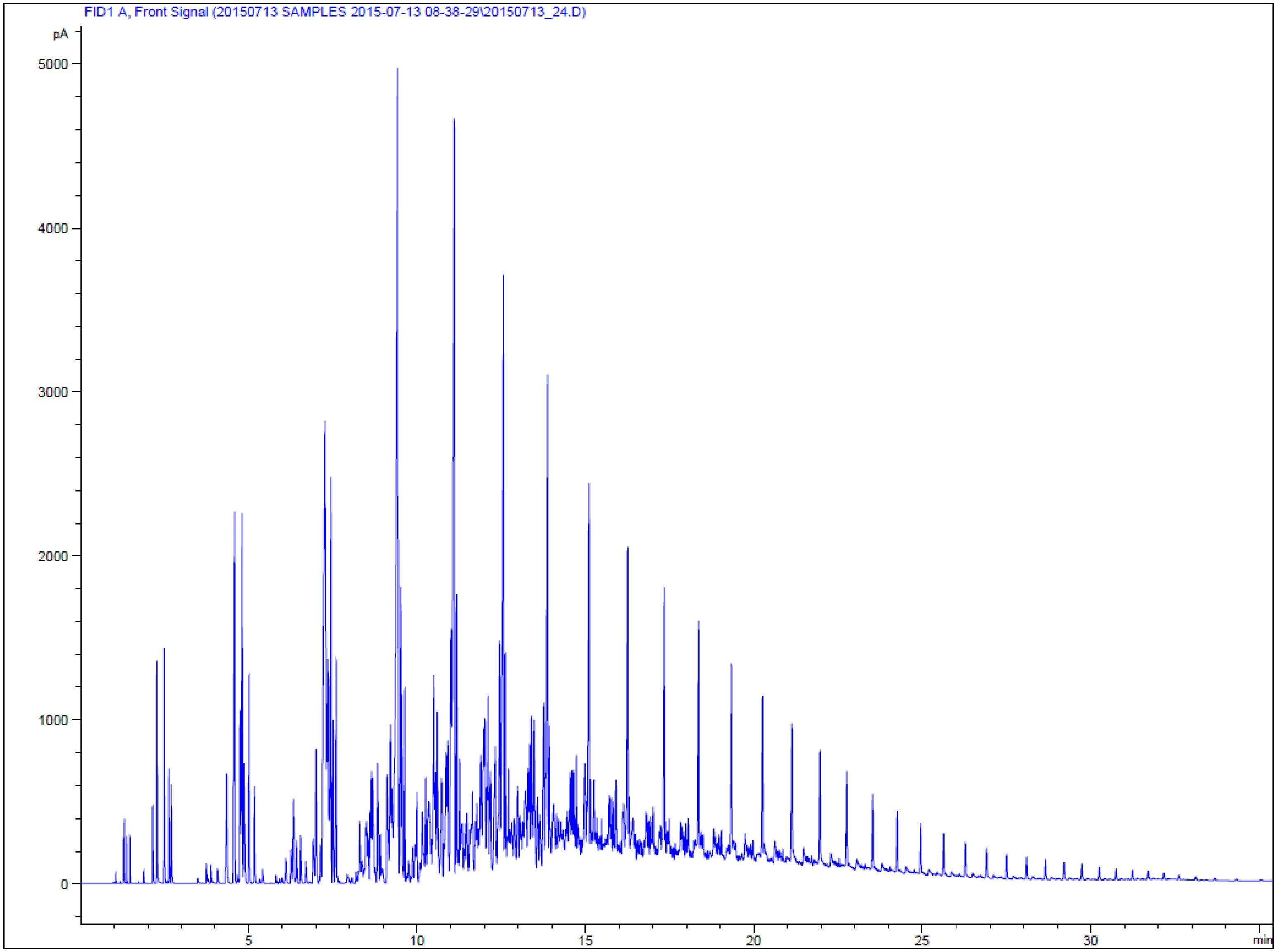

Figure A6: Simulated distillation chromatograph for sample CBTL103115-24

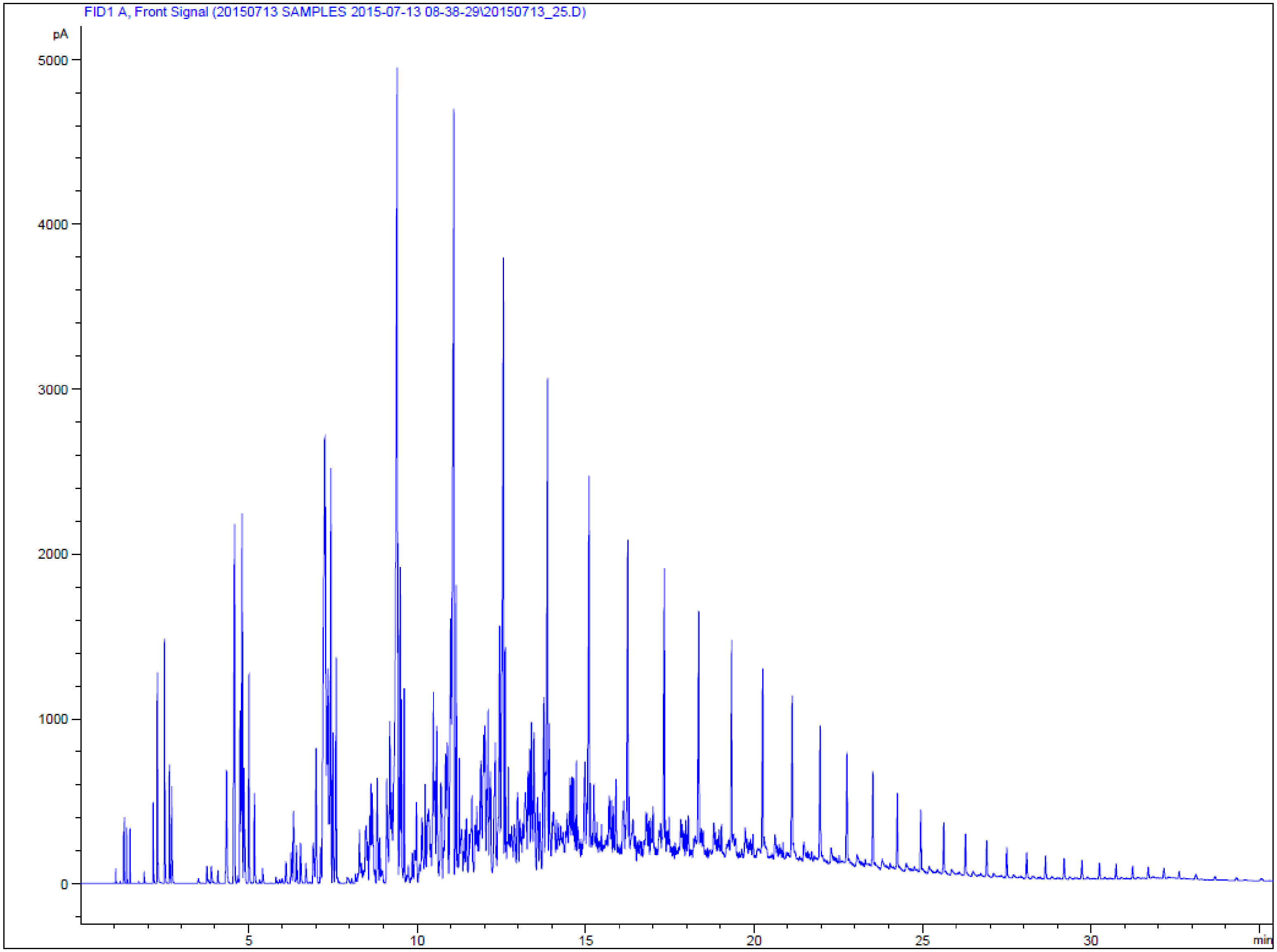

Figure A7: Simulated distillation chromatograph for sample CBTL110215-14

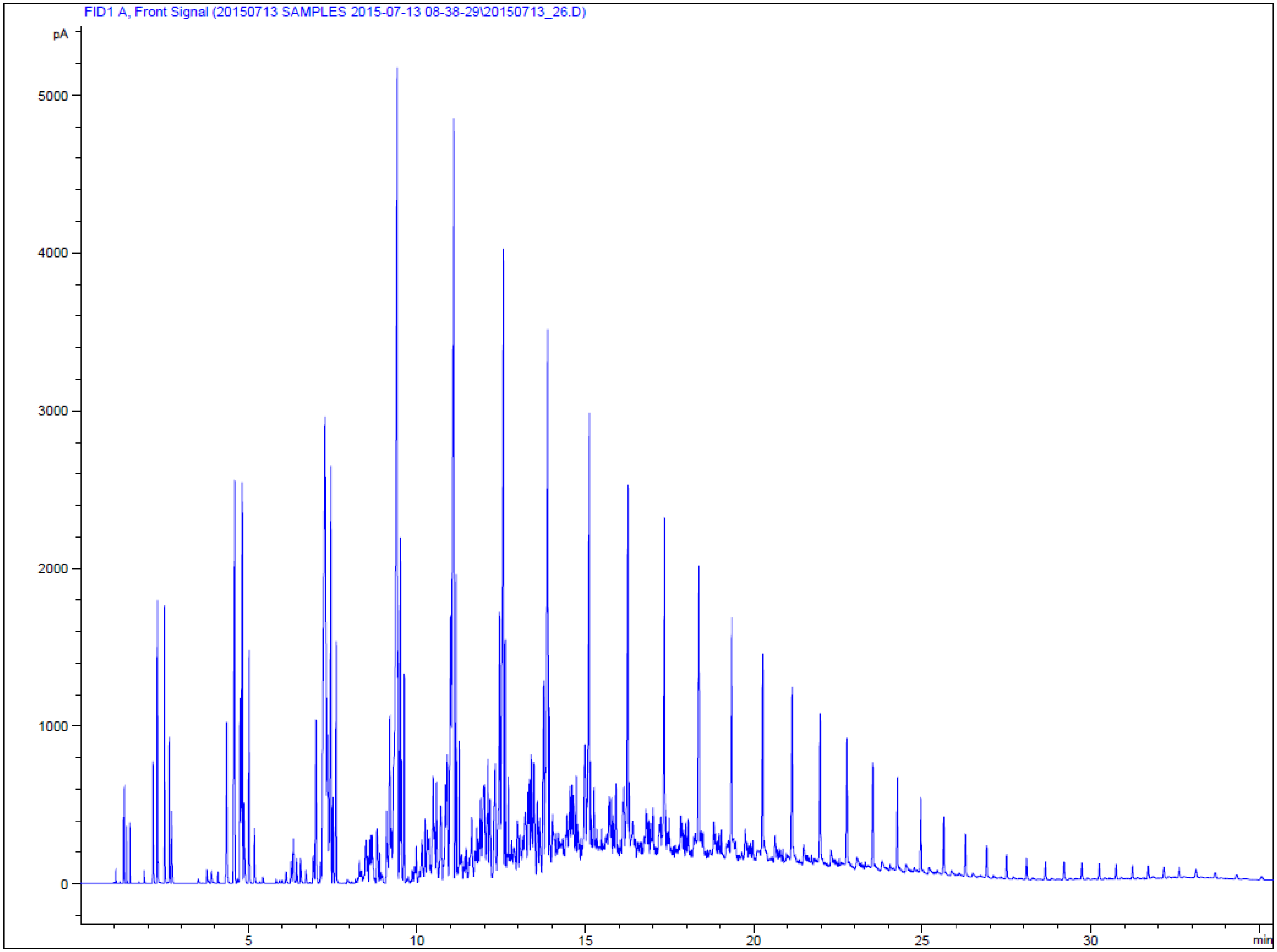

Table A6: GCMS of organic fraction of decanted samples produced on bottled syngas only

Sample No.	CBTL102415-04		CBTL102615-08	
Syngas Composition	Bottles Only		Bottles Only	
Set Pressure (psi)	280		200	
Set Temp. (°C)	240		240	
Hydrocarbon Carbon Number				
Carbon #	Alkane	Branched/ Other	Alkane	Branched/ Other
C7	2.9%	2.0%	2.8%	2.9%
C8	3.8%	5.6%	3.7%	6.6%
C9	3.5%	6.6%	3.4%	8.0%
C10	3.0%	6.5%	2.8%	7.6%
C11	2.8%	6.4%	2.0%	7.4%
C12	2.1%	6.6%	1.7%	6.5%
C13	2.0%	5.8%	1.6%	5.5%
C14	2.1%	4.9%	1.5%	4.5%
C15	1.7%	4.1%	1.3%	3.6%
C16	1.5%	3.6%	1.2%	3.0%
C17	1.4%	2.6%	1.1%	2.4%
C18	1.2%	2.0%	0.9%	1.8%
C19	1.1%	1.5%	0.8%	1.3%
C20	1.0%	1.0%	0.6%	0.9%
C21	0.8%	0.8%	0.5%	0.5%
C22	0.7%	0.5%	0.4%	0.4%
C23	0.6%	0.4%	0.4%	0.3%
C24	0.5%	0.3%	0.4%	1.3%
C25+	2.2%	3.9%	1.8%	6.3%

Figure A8: GCMS chromatograph for sample CBTL102415-04

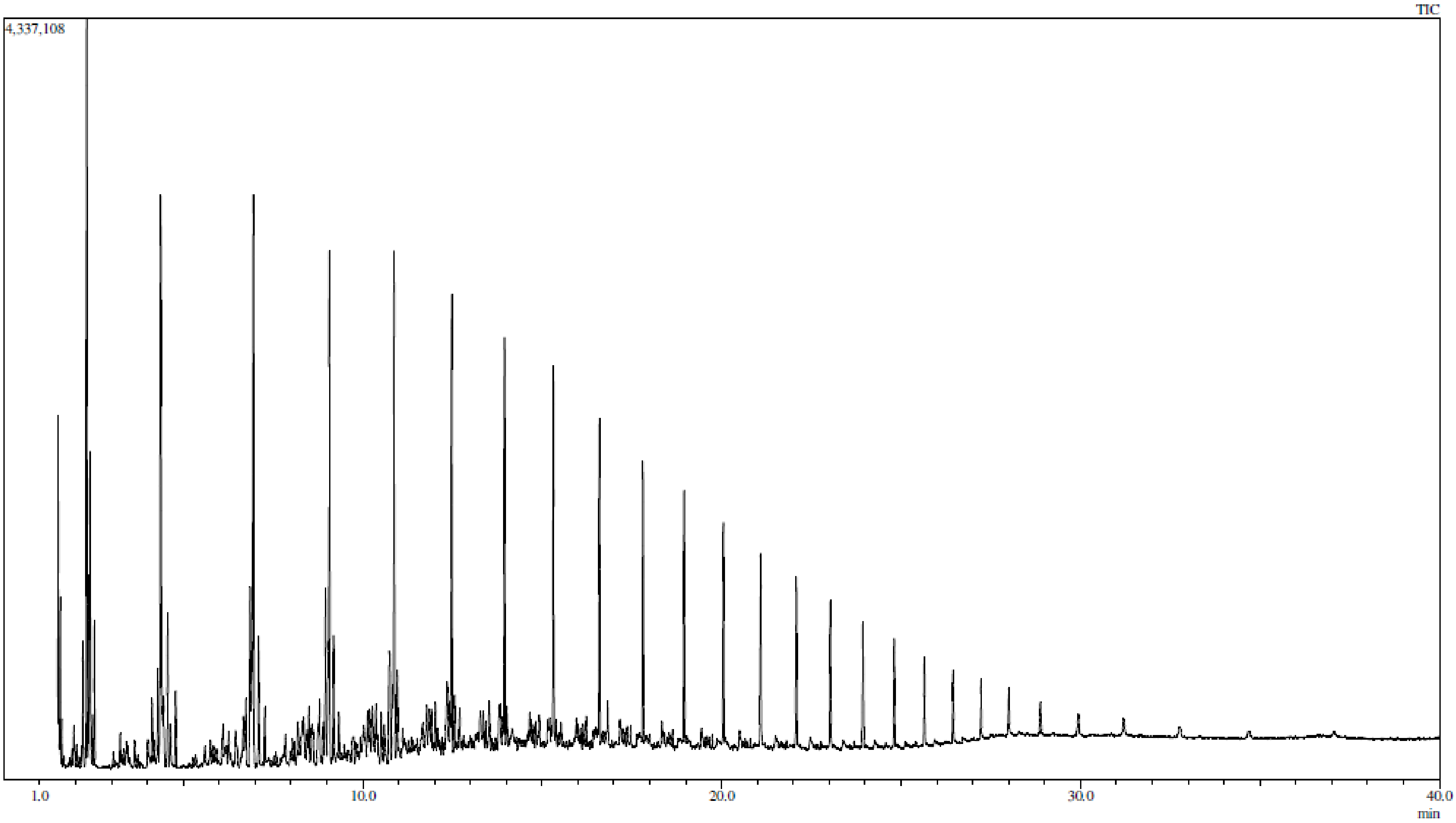

Figure A9: GCMS chromatograph for sample CBTL102615-08

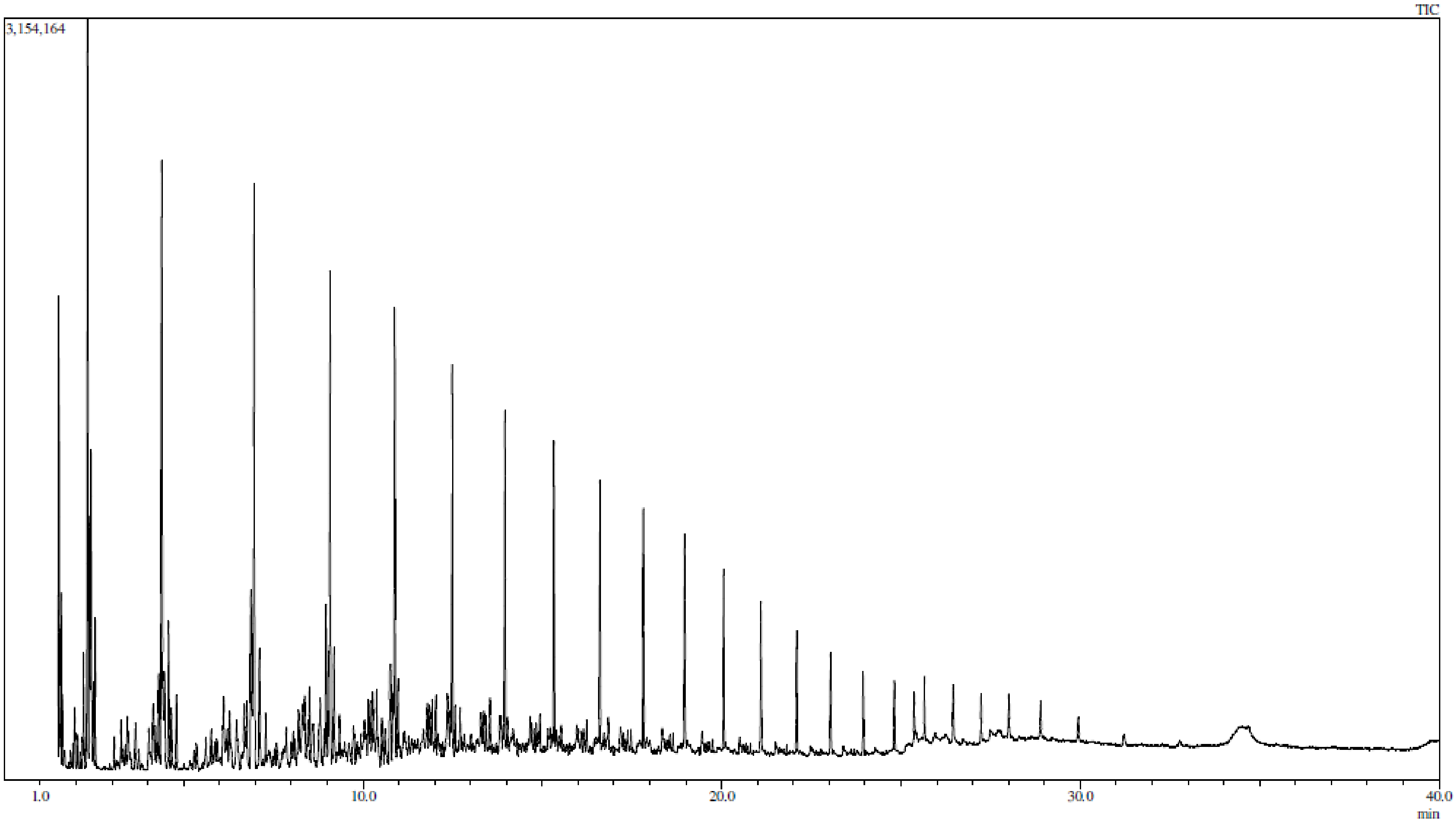

Table A7: GCMS of organic fraction of decanted samples produced on bottled and coal derived syngas

Sample No.	CBTL102715-24		CBTL102815-24	
Syngas Composition	Bottled & Coal Gas		Bottled & Coal Gas	
Set Pressure (psi)	185		185	
Set Temp. (°C)	240		240	
Hydrocarbon Carbon Number				
Carbon #	Alkane	Branched/ Other	Alkane	Branched/ Other
C7	2.8%	3.1%	2.2%	1.6%
C8	3.8%	6.7%	3.0%	5.2%
C9	3.5%	8.0%	2.8%	6.5%
C10	2.8%	7.8%	2.4%	6.4%
C11	2.1%	7.7%	2.1%	6.1%
C12	1.8%	6.7%	1.5%	5.7%
C13	1.6%	5.7%	1.4%	4.8%
C14	1.5%	4.6%	1.2%	4.1%
C15	1.3%	3.8%	1.1%	3.5%
C16	1.2%	3.4%	1.0%	3.1%
C17	1.1%	2.5%	0.9%	2.4%
C18	0.9%	2.1%	0.8%	1.9%
C19	0.8%	1.5%	0.8%	1.6%
C20	0.6%	1.0%	0.6%	1.2%
C21	0.5%	0.7%	0.5%	0.9%
C22	0.4%	0.5%	0.4%	0.7%
C23	0.3%	0.4%	0.3%	0.6%
C24	0.3%	0.8%	0.3%	0.6%
C25+	1.3%	4.8%	2.6%	17.0%

Figure A10: GCMS chromatograph for sample CBTL102715-24

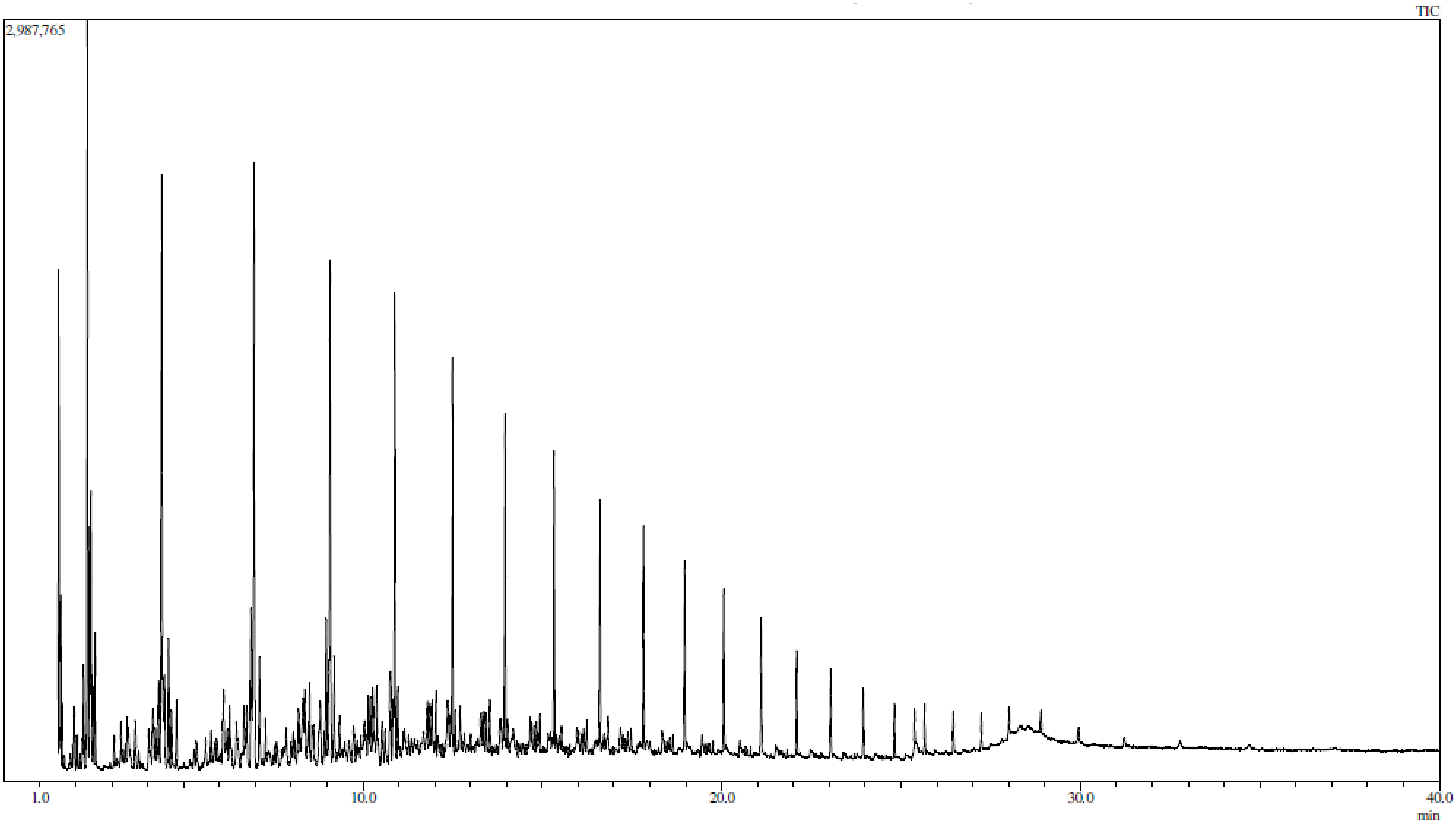

Figure A11: GCMS chromatograph for sample CBTL102815-24

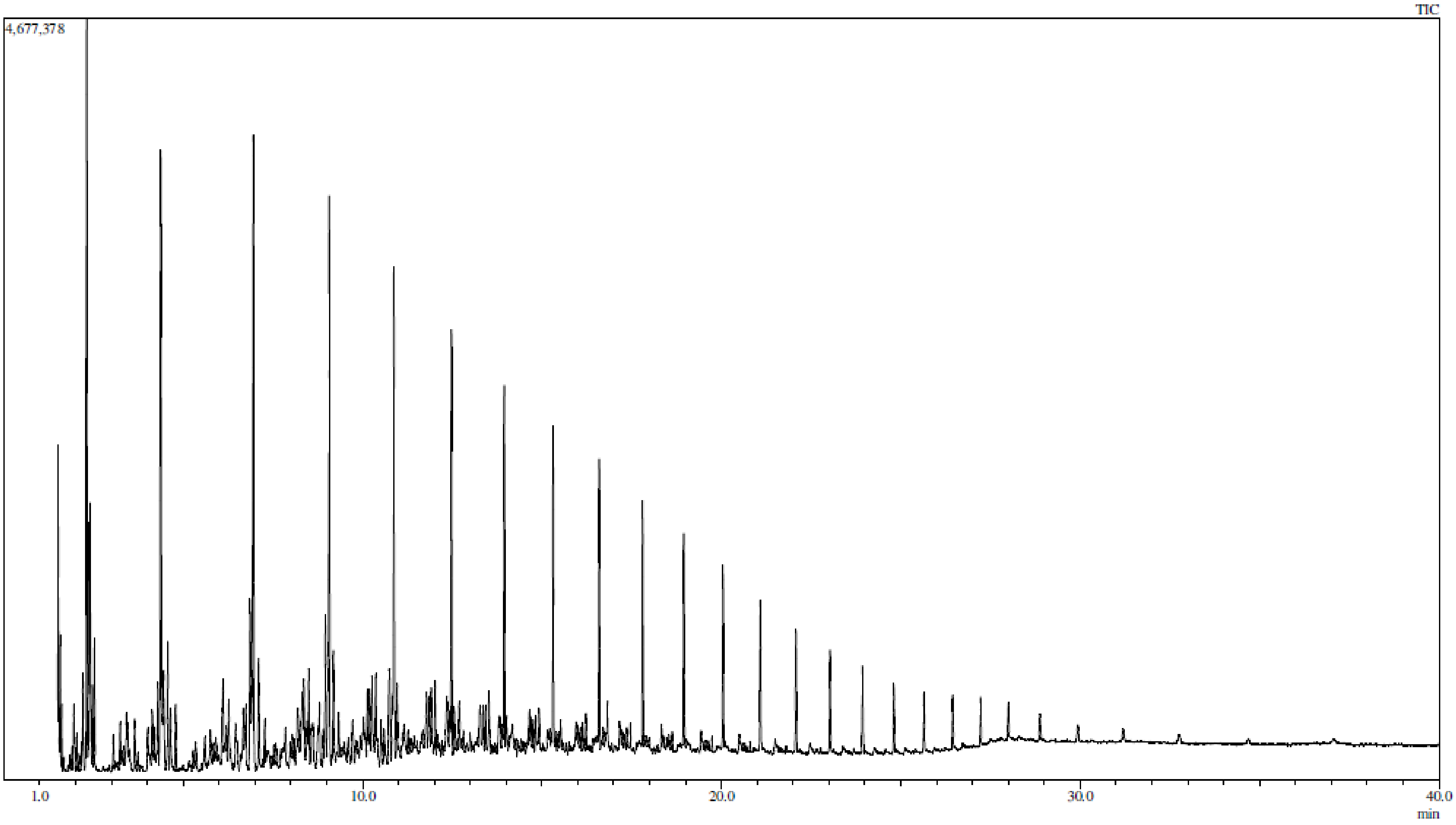

Table A8: GCMS of organic fraction of decanted samples produced on bottled and coal/biomass derived syngas

Sample No.	CBTL103015-24		CBTL103115-24	
Syngas Composition	Bottled & Coal/Biomass Gas		Bottled & Coal/Biomass Gas	
Set Pressure (psi)	185		185	
Set Temp. (°C)	240		240	
Hydrocarbon Carbon Number				
Carbon #	Alkane	Branched/ Other	Alkane	Branched/ Other
C7	2.8%	2.3%	2.6%	1.1%
C8	3.7%	6.7%	3.5%	6.5%
C9	3.4%	8.1%	3.3%	7.7%
C10	2.8%	7.8%	2.7%	7.6%
C11	2.4%	7.3%	1.9%	7.1%
C12	1.7%	6.5%	1.6%	6.0%
C13	1.5%	5.4%	1.5%	4.8%
C14	1.4%	4.5%	1.5%	4.2%
C15	1.3%	3.6%	1.4%	3.7%
C16	1.2%	3.3%	1.3%	3.5%
C17	1.1%	2.6%	1.3%	3.0%
C18	1.0%	2.0%	1.2%	2.6%
C19	0.9%	1.5%	1.1%	2.0%
C20	0.7%	1.1%	0.9%	1.6%
C21	0.5%	0.7%	0.7%	1.2%
C22	0.4%	0.6%	0.6%	0.9%
C23	0.4%	0.4%	0.5%	0.6%
C24	0.3%	0.3%	0.5%	1.2%
C25+	1.5%	6.4%	1.4%	3.4%

Figure A12: GCMS chromatograph for sample CBTL103015-24

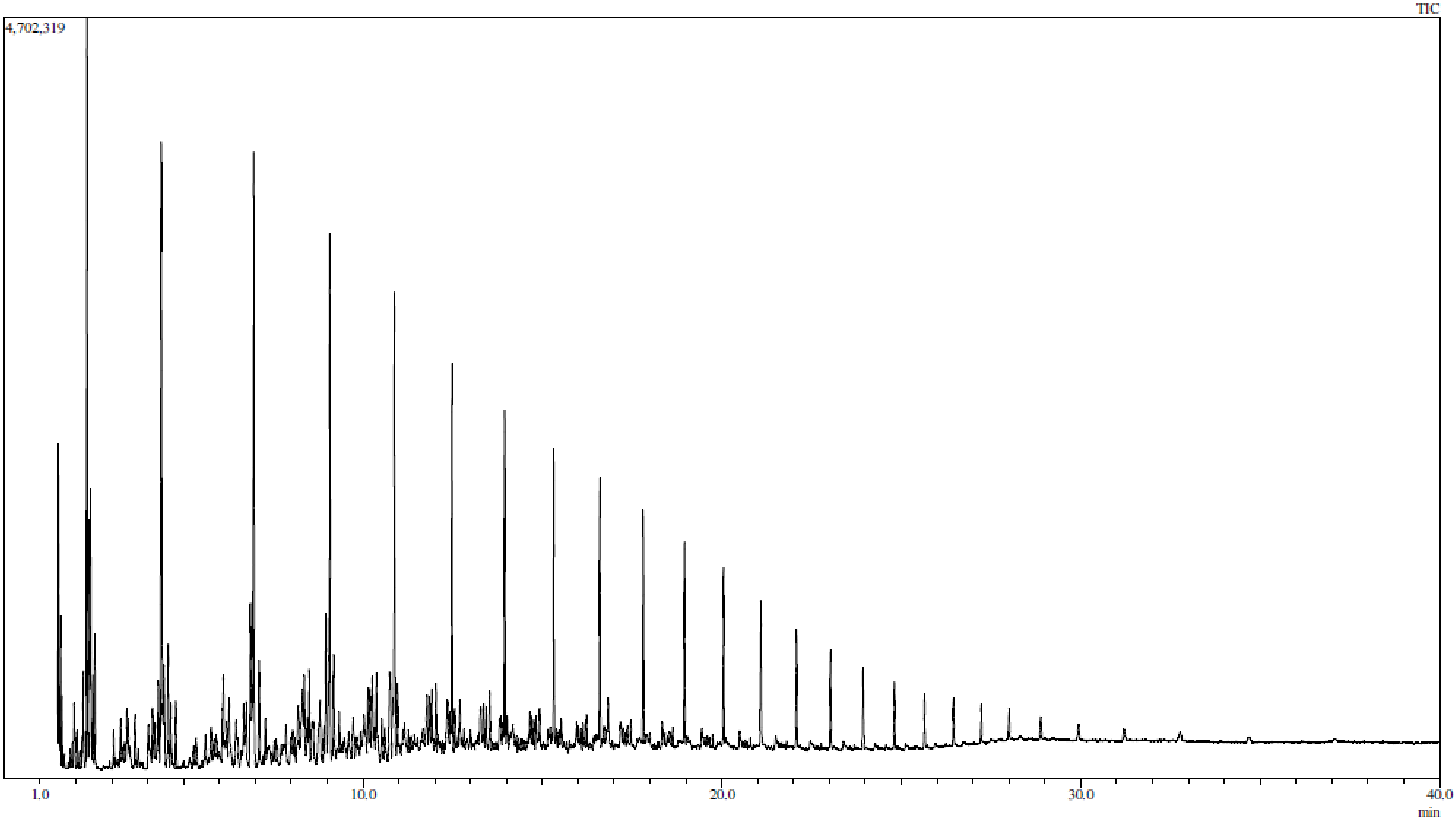

Figure A13: GCMS chromatograph for sample CBTL103115-24

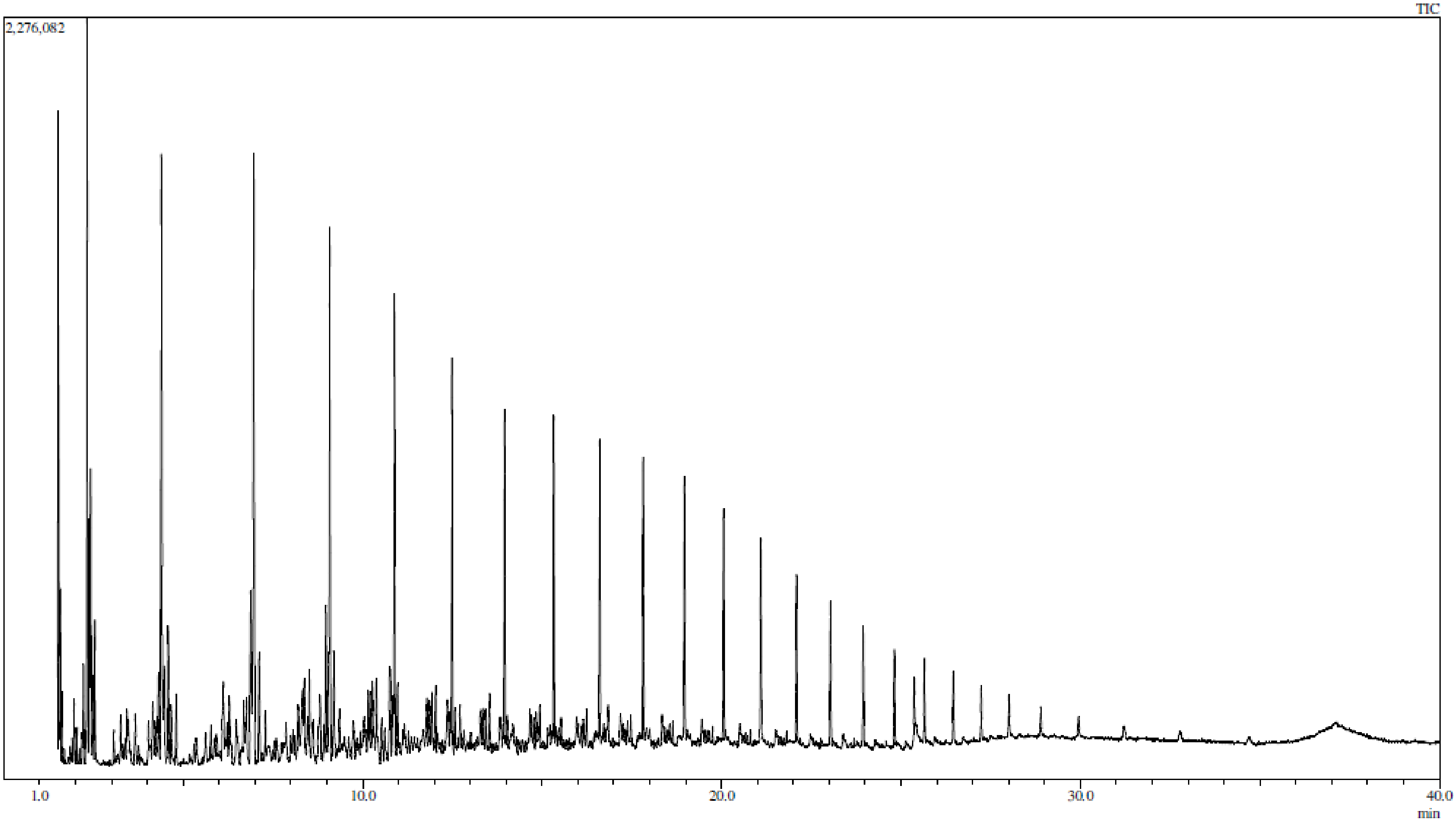

Table A9: GCMS of organic fraction of decanted samples produced on bottled syngas only

Sample No.	CBTL110215-14	
Syngas Composition	Bottles Only	
Set Pressure (psi)	280	
Set Temp. (°C)	240	
Hydrocarbon Carbon Number		
Carbon #	Alkane	Branched/ Other
C7	2.5%	1.8%
C8	3.4%	4.5%
C9	3.2%	5.3%
C10	2.8%	5.4%
C11	2.6%	5.5%
C12	2.0%	5.6%
C13	1.9%	5.1%
C14	1.8%	4.6%
C15	1.6%	4.0%
C16	1.4%	3.7%
C17	1.4%	2.8%
C18	1.2%	2.2%
C19	1.1%	1.8%
C20	0.9%	1.2%
C21	0.8%	1.0%
C22	0.6%	0.8%
C23	0.5%	0.6%
C24	0.4%	0.5%
C25+	2.4%	11.1%

Figure A14: GCMS chromatograph for sample CBTL110215-14

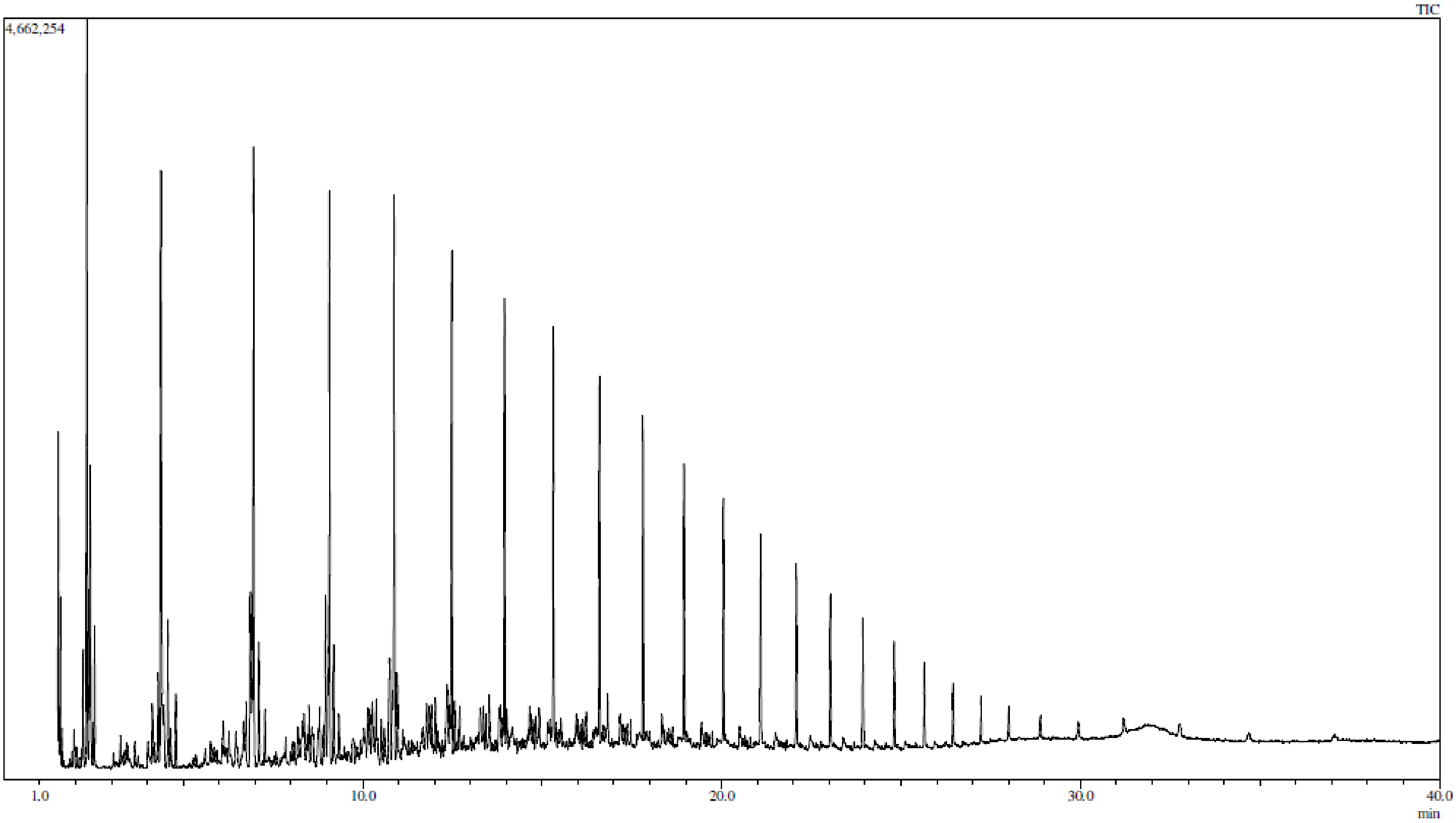

Table A10: Ultimate analysis of feed coal and feed biomass

	Coal	Biomass
Carbon	55.7	47.2
Hydrogen	5.4	5.8
Nitrogen	1.6	1.3
Oxygen, Ash, Sulfur, etc*	37.4	45.7

* by difference

Table A11: Proximate analysis of feed coal

	1/5 001	1/5 002	1/6 001	1/6 002	1/8 001	Average
Moisture	19.1%	20.2%	19.2%	11.3%	19.4%	17.8%
Volatile Carbon	36.2%	28.3%	29.1%	35.6%	32.6%	32.4%
Fixed Carbon	38.3%	45.2%	45.4%	46.1%	42.4%	43.5%
Ash	6.4%	6.3%	6.3%	7.0%	5.6%	6.3%

Table A12: Proximate analysis of feed biomass

	1/6 001	1/6 002	1/8 001	Average
Moisture	7.1%	7.2%	7.0%	7.1%
Volatile Carbon	71.4%	70.5%	74.3%	72.1%
Fixed Carbon	20.7%	21.5%	18.1%	20.1%
Ash	0.8%	0.7%	0.5%	0.7%