



Catalytic conversion wood syngas to synthetic aviation turbine fuels over a multifunctional catalyst

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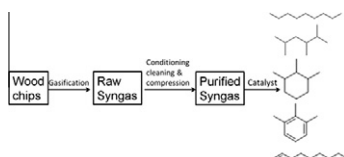
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HIGHLIGHTS

- ▶ A continuous process was developed to make synthetic aviation turbine fuels from biomass.
- ▶ The process involved gasification, syngas cleaning, and Fischer–Tropsch synthesis.
- ▶ Synthetic aviation turbine fuels were produced from syngas over a multi-functional catalyst.

GRAPHICAL ABSTRACT

Synthetic aviation turbine fuels were produced from wood syngas over a multi-functional catalyst.



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ABSTRACT

A continuous process involving gasification, syngas cleaning, and Fischer–Tropsch (FT) synthesis was developed to efficiently produce synthetic aviation turbine fuels (SATFs). Oak-tree wood chips were first gasified to syngas over a commercial pilot plant downdraft gasifier. The raw wood syngas contains about 47% N₂, 21% CO, 18% H₂, 12% CO₂, 2% CH₄ and trace amounts of impurities. A purification reaction system was designed to remove the impurities in the syngas such as moisture, oxygen, sulfur, ammonia, and tar. The purified syngas meets the requirements for catalytic conversion to liquid fuels. A multi-functional catalyst was developed and tested for the catalytic conversion of wood syngas to SATFs. It was demonstrated that liquid fuels similar to commercial aviation turbine fuels (Jet A) was successfully synthesized from bio-syngas.

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1. Introduction

Biomass-derived fuels are becoming more popular due to the rising costs of fossil fuels as well as concerns of national security and the national economy. A wide range of fuels and chemicals can be produced from biomass, including gasoline, diesel, heating fuel, jet fuel, synthetic natural gas, and oxygenates (Huang et al., 2012; Che et al., 2012). Aviation turbine fuels (ATFs) are a complex mixture of C₈–C₁₇ hydrocarbons, which include paraffins, isoparaffins, aromatics and naphthenes (Huber et al., 2006). They are currently produced from the kerosene fraction of petroleum

distillation and hydro-processing of heavier fraction of the petroleum (Wright et al., 2008). In the past decades, many efforts have been performed on production of ATF from shale, coal, and tar sands (Daggett et al., 2008). Shale-derived JP-4 has been tested and demonstrated using aviation engines, and no harmful consequences were found (Edwards, 2003). No negative impact was found on engine operation when using syngas-based Jet fuels (Moses et al., 1997). Since almost all the ATFs are from the non-renewable petroleum, it is necessary to find a sustainable route for producing SATFs. The most highly developed and technically proven route for producing alternative fuels from lignocellulosic biomass involves the gasification process. Syngas is produced, cleaned, and then catalytically converted via Fischer–Tropsch synthesis (FTS) or CO hydrogenation (alcohol synthesis). The products

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are then upgraded to sequester the desired products (Leckel, 2009a).

Currently, FT-based catalysts including iron and cobalt catalysts have been used to produce long-chain paraffins from syngas. These products undergo hydrotreating and/or the hydrocracking process to upgrade these long-chain paraffins to the desired range of ATFs or jet fuels. In order to meet the requirement of the freezing point (-40 to -47 °C) and other important specifications of commercial ATF (Jet A) and military ATF (JP-8), aromatics and/or naphthenes should be increased in the FTS-derived ATF fraction (Huber et al., 2006; Dupain et al., 2005). Multiple processing steps of FTS liquids are required to reach these specifications of Jet A and JP-8 (Huber et al., 2006; Leckel, 2009a and Forest and Muzzell, 2005). However, too many processing steps will increase the cost of the product and decrease the overall efficiency of the process. Therefore, it is significant to explore simple processes over a multi-functional catalyst for the creation of SATFs through FTS (Forest and Muzzell, 2005). Many studies have been carried out to synthesize liquid fuels using high quality syngas (mainly CO and H₂) with a low nitrogen composition (Yan and Yu, 2012), which is mainly derived from natural gas or coal. There are a limited number of publications using nitrogen-rich, high CO₂ syngas to produce hydrocarbons (Yan and Yu, 2012). The existing downdraft gasifier at Mississippi State University is producing syngas from biomass (known as producer gas). Currently, the producer gas contains about 18% hydrogen, 21% CO, 12% CO₂, 2% CH₄ and 47% N₂ (Yan and Yu, 2012). The nitrogen and carbon dioxide contents are too high for economic hydrocarbon synthesis using existing catalyst technologies. Developing high activity and high stability catalysts is essential for better overall performance when using producer gas. In this study, a continuous process including catalyst preparation, gasification, syngas cleaning, and FTS was developed to demonstrate biomass to liquid (BTL) fuel technology. A multi-functional catalyst was designed and tested for the catalytic conversion of producer gas derived from wood to form SATFs. The activity, selectivity, stability, and life-time of the catalyst were evaluated. The liquid product was analyzed and compared to fuel Jet A.

2. Experimental

2.1. Preparation of syngas from wood chips

Oak-tree wood chips were used as the feedstock for the gasification process. Their moisture content was analyzed with an OHAUS MB200 balance (Certified Scale, Inc., Menomonee Falls, WI). The sample weight was measured at room temperature. The sample was heated to and held at 160 °C until a constant value was obtained (changes < 0.01 g in 60 s). The percent of weight loss was regarded as the moisture content. Wood chips with a moisture content of 8.3–10.8% were used in this research for material and energy balance analysis.

The producer gas composition was analyzed with an Agilent 6890N GC (Santa Clara, CA), with a TCD detector, and argon was used as the carrier gas. The process temperatures were obtained from the host computer, which acquired the data from thermocouples. The volume concentrations of main syngas components were monitored online by a portable gas analyzer (7900P4C, NOVA Analytical Systems, Inc., Niagara Falls, NY).

The pilot-plant scale downdraft gasifier, BioMax 25, was purchased from Community Power Corporation (Littleton, CO). The automatic gasification system used a host computer to control the gasification process. Its main components included the feeding system, the gasifier, the heat exchanger and the filters. There were multiple thermocouples and pressure transducers installed in the system to monitor the running of the gasification system. The

producer gas flow rate was set at 65 Nm³/h. The computer program would adjust the air injection rate and wood chip feeding rate according to the setting producer gas flow rate.

An auger feeding system was installed with the gasifier. When the fuel level in the gasifier fell below the set-point, the motor of the feeder would be activated. The gasifier was designed with five levels of air injection loops, and each loop had six injection points into the gasifier. This ensured that the air was distributed into the gasifier evenly at the same level. The amount and rate of air injection were controlled by the computer and varied according to the temperatures inside the gasifier.

The heat exchanger cooled the producer gas from 500–700 °C to about 110 °C. This system used ambient air to cool the producer gas. The producer gas then went through parallel bag filters to remove fine particles. After filtration, the producer gas then went through a filter with activated carbon to remove tars. The effluent producer gas contained about 47% N₂, 21% CO, 18% H₂, 12% CO₂, 2% CH₄, some water vapor and trace amount of other gases. The cool syngas was then compressed to a storage tank or sent to a burner. Mass balance and carbon balance were performed based on wood chip feeding rate, inlet air flow rate, outlet gas flows, gas composition analysis, solid char weight and composition analysis. The ashes and tars that were trapped inside the gasification system were neglected when calculating the material.

2.2. Cleaning and compression of wood syngas

The producer gas was first compressed to approximately 0.31 MPa. After compression, a water scrubber and gas drying apparatus were assembled to scrub the producer gas. Two 25-gallon 304 stainless steel (SS) wide mouth tanks were connected for the water scrubber. The first tank was outfitted with 13 SS exhaust mufflers with a filtration rating of 50 μ. These mufflers were used to create the maximum amount of gas bubbles so that the utmost possible surface area of producer gas could come in contact with the water, and contaminants, e.g., ammonia, could be scrubbed by dissolving in the water. After the water scrubber process, the gasifier syngas was flowed through another 25-gallon tank which contained 36 kg of silica gel desiccant to remove moisture in the producer gas. Finally, the producer gas was compressed to approximately 13.8 MPa using a 2-stage pneumatic air pump obtained from Hydraulics International (Chatsworth, CA).

2.3. Deep purification of the compressed producer gas

A syngas purification process was designed after indentifying the possible poisoning or negative components for the FTS process, e.g., moisture, oxygen, sulfur, ammonia and tar. The catalysts and adsorbents were selected from alumina-supported metal catalysts, molsieve 13X, active carbon, silica gel and other high surface area materials. These catalysts and adsorbents were loaded into reactors in series. The reactor system was built with controlling parameters of temperature, pressure, and flow rate. The pilot-plant scale cleaning unit is built in the Pace Seed Laboratory of Mississippi State University. The cleaned syngas should meet the basic requirements for the following step of catalytic conversion to liquid fuels and chemicals. These specifications include a sulfur content (H₂S + COS) of less than 10 ppb, and ammonia content (NH₃) of less than 1 ppm, and an oxygen content of less than 1 ppm (Yan and Yu, 2012).

2.4. Preparation of Fe promoted K–Co–Mo–γ-Alumina catalysts

γ-Alumina (surface area, 246 m²/g, pore volume, 1.15 mL/g) was used as the support for the preparation of Fe promoted K–Co–Mo–γ-Alumina catalysts. The weight percent of Mo, Co, K and

Fe was specified with the corresponding catalyst. Ammonium heptamolybdate, cobalt nitrate, iron nitrate, and potassium carbonate (all are from Sigma–Aldrich Company) were used as precursors for Mo, Co, Fe, and K, respectively.

The catalyst samples were prepared by an aqueous incipient-wetness impregnation technique. The alumina pellets were first ground to 20–50 mesh before impregnation. The required amount of ammonium heptamolybdate was dissolved in water. Then, impregnation was done at 80 °C, dried at 120 °C for 4 h, and then calcined at 350 °C for 2 h at a heating rate of 5 °C/min. Next, the required amount of cobalt nitrate (aqueous solution) was impregnated at 80 °C over the Mo/ γ -Al₂O₃, dried at 120 °C for 4 h, and calcined at 350 °C for 2 h at a heating rate of 5 °C/min. Then, similarly, the required amount of iron nitrate (aqueous solution) was impregnated over the Co/Mo/ γ -Al₂O₃ material at 80 °C, dried at 120 °C for 4 h, and calcined at 350 °C for 2 h at a heating rate of 5 °C/min. Finally, potassium carbonate was dissolved in water and impregnated with the Fe/Co/Mo/ γ -Al₂O₃ material, dried at 120 °C for 4 h, and calcined at 400 °C for 5 h. Metal loadings of the catalyst sample were 5 wt.% molybdenum, 3 wt.% cobalt, 5 wt.% iron, and 3 wt.% potassium.

2.5. Catalytic reaction

The synthesis gas conversion reaction was carried out in a continuous flow fixed-bed reactor system. Three (3) grams of the catalyst was loaded to the reactor. The system was first purged by a helium flow for 30 min, followed by pre-reducing stage with a syngas mixture at 400 °C for 8 h, then producer gas was fed into the system until reaching the desired pressure by slowly adjusting the system to the desired temperature. The reaction was operated under the following conditions: 250–350 °C, a gas hourly space velocity (GHSV) of 500–5,000 h^{−1} and a pressure of 3.14–8.62 MPa. Mass balance and carbon balance were performed based on inlet/outlet flows, gas composition analysis and liquid product weight and composition.

2.6. Analysis of gas and liquid products using GC and GC/MS

The analysis of gas phase product has been carried out with an on-line Agilent 7890 gas chromatograph provided with two thermal conductivity detectors (TCD) and a flame ionization detector (FID). Helium and nitrogen were used as the carrier gases.

Liquid products were collected using a condenser kept at −3 °C. Liquid samples were analyzed using an Agilent 7683B Series Injector coupled to an Agilent 6890 Series gas chromatograph system and a 5973 Mass Selective Detector, i.e., a quadrupole type GC–MS system, as well as a FID detector. An Agilent DB-WAXetr (50 m × 0.32 mm I.D., 1.0 μ m) capillary column was used. A constant column flow of 1 mL/min (24 cm³/s) helium was applied. The injector was kept at 250 °C. Samples were injected (1 μ L) with a split ratio of 100:1. The temperature-programmed separation started at 40 °C for 5 min, and then the temperature was increased at a rate of 10 °C/min to 250 °C for 10 min. The FID detector worked at a temperature of 250 °C with helium makeup gas at 30 mL/min. For the MS, the transfer line and EI source temperature were 250 and 200 °C. Quadrupole conditions involved an electron energy of 70 eV and an emission current of 150 μ A. The syncrude samples were dried using sodium sulfate and subjected to an engine knock test (ASTM D2699; D2700), API gravity test, distillation range test (ASTM D86) and Reid vapor pressure test (ASTM 5191). The distilled syncrude samples with a boiling point between 110 and 310 °C were collected and analyzed. The distillation column and procedure which was used are described in ASTM's standard test method D2892. A commercial Jet A sample was also analyzed to compare to the liquid samples derived from the producer gas.

2.7. Detailed hydrocarbon analysis (DHA) of liquid hydrocarbons

Detailed hydrocarbon analysis (DHA) was performed over a Perkin Elmer Clarus 680 GC with a FID detector using the PIANO method. PIANO describes the method for determining the amount of paraffins (P), iso-paraffins (I), aromatics (A), naphthenes (N), and olefins (O) within a sample. A liquid sample with a volume of 1 μ L was injected into a 100-meter GC column with about 200:1 split ratio. A flame ionization detector and retention time library was used to identify compounds with a carbon number up to 14. This method is based on ASTM test method D 5134–92 but uses a 100-meter capillary column instead of a 50-meter column. The PIANO method is mainly used for gasoline-type samples, which is why it is limited to compounds with carbon numbers less than 14. Any C15 compounds or heavier were reported as unknown compounds. The initial temperature of the GC injector was set at 200 °C and held at this temperature for 43.15 min. The sample injector of the GC was heated to 450 °C at 100 °C/min and held at this temperature throughout the end of the test. A DHA analytical column (100 m × 0.25 μ m I.D.) was used to separate sample components. Hydrogen was used as a carrier gas with a flow rate of 100 mL/min. The initial oven temperature was held at 35 °C for 5 min, heated to 50 °C at 10 °C/min and held for 21.5 min. Then, the oven temperature was ramped to 150 °C with a heating rate of 3 °C/min and kept at 150 °C for 4.67 min. The FID detector temperature was 250 °C with a hydrogen flow rate of 42 mL/min and an air flow rate of 450 mL/min.

3. Results and discussion

3.1. Design of multifunctional catalysts for jet fuel synthesis from wood derived syngas

Paraffins, iso-paraffins, aromatics, and naphthenes are the main hydrocarbon components in jet fuel, while straight chain paraffins and/or olefins are the main products over iron and cobalt-based FT catalysts (Leckel, 2009a,b). Multiple processing steps are usually followed after FTS to reach these specifications of Jet fuel (Huber et al., 2006). However, too many processing steps will increase the cost of the product and decrease the overall efficiency of the process. Therefore, to explore fewer steps for synthesizing ATF via FTS that meets all these specifications, new catalysts are needed to produce the desired range of ATFs or jet fuels from syngas. One of the alternatives to improve the selectivity and quality limitations of the FT process is to use hybrid or composite catalysts which comprise a FT base catalyst and a co-catalyst containing the appropriate functionality to increase the yield and selectivity of the desired products. The combination of an iron-based FT catalyst displaying high selectivity to olefins and oxygenates with ZSM-5 or HY zeolites (Botes, 2005; Yan et al., 2008) results in an enhanced gasoline selectivity and an increased concentration of high-octane branched and aromatic hydrocarbons by promoting oligomerization, cracking, isomerization, and aromatization reactions on the zeolite acid sites. Another approach is to convert syngas to alcohols over an alcohol synthesis catalyst, and alcohols subsequently convert to hydrocarbons over solid acid catalysts like ZSM-5 (Yan et al., 2008).

Multifunctional catalysts are needed to chemically convert syngas to jet fuel range hydrocarbons like paraffins, iso-paraffins, aromatics, and naphthenes; therefore, the catalyst should include CO hydrogenation, FTS, alcohol dehydration, and hydrotreating/hydrocracking activity. As mentioned previously, bio-syngas (producer gas) will be used as sole feedstock in the process. In the designed process, alcohols are formed from syngas by CO hydrogenation. Hydrocarbons are produced from syngas through

alcohol dehydration and/or the FTS process over heterogeneous catalysts. The designed catalyst has functions of CO hydrogenation for alcohol formation, FTS for paraffin production, and alcohol dehydration for producing iso-paraffins, aromatics, naphthenes from alcohols. The isomerization function is also needed since branched paraffins are the favored component for jet fuels, while FTS and alcohol synthesis processes are principally used for producing linear hydrocarbon molecules (Gujar et al., 2009). Branched paraffins, aromatics, naphthenes and/or iso-alcohols are produced from their linear counterparts by the isomerization process.

Alcohols are synthesized from syngas through the CO hydrogenation process. Various catalyst systems, such as modified Cu/ZnO, modified MoS₂, and modified Fe or Co FT catalysts, have been found to produce higher alcohols from syngas (Freerks and Muzzell, 2004). Cobalt-promoted Mo based catalysts have been extensively used in the hydrotreating process (Davis, 2005), and it was also reported Co–Mo based bimetallic catalysts were active to produce mixed higher alcohols from syngas (Ancheyta-Jua-Arez et al., 1999). C1–C7 mixture alcohols were produced from syngas over Co–Mo based catalysts (Bian et al., 1999).

Only Fe, Co, Ni and Ru metals have sufficiently high activities for the FTS process (Li et al., 1998). Among these four metals, only cobalt and iron-based catalysts can be considered as practical FT catalysts (Li et al., 1998). Co catalysts are generally 5–10 times more active than iron catalysts for comparable conditions. Moreover, carbon selectivities to C₅⁺ of Co catalysts are also generally higher relative to Fe catalysts, since Co produces very little or no CO₂. Co is already used as the alcohol synthesis active component, so iron is also selected for the designed catalyst due to its low cost, low H₂/CO usage ratio (near 0.7), and tendency to yield high amounts of olefins in hydrocarbon distribution. Iron can also be operated at high temperatures (>300 °C).

One of the alternative ways to synthesize hydrocarbons is by the condensation of alcohols. This is a process in which alcohols lose water and form olefins and/or cyclic hydrocarbons and/or aromatics. Alcohol dehydration reactions generally occur by heating the alcohol with strongly acidic zeolites and oxides like SiO₂, Al₂O₃, TiO₂, ZrO₂, and ZnO. These have been extensively used as heterogeneous catalysts for alcohol dehydration to hydrocarbons (Davis, 2007). Our previous work on conversion of alcohols to hydrocarbons demonstrated that the methanol reaction over H⁺/ZSM-5 produced aromatics including *p*-xylene, 1,2,3-trimethylbenzene, and 1,2,4,5-tetramethylbenzene and oxygenates including dimethyl ether, 3-methyl-2-butanone, and acetone among others (Gujar et al., 2009). The reaction of ethanol under similar conditions produced ethyl-substituted aromatic compounds including 1, 3-diethylbenzene and 1,2-diethylbenzene and alkanes like 3-methylheptane and 4-methyloctane among others. When ethanol was used, the production of oxygenates was less than that obtained for methanol. When 1-propanol reacted over H⁺-ZSM-5, products exclusively composed of alkenes and branched alkanes like 2-methyl-1-propene, 4-methylhexane, and 4-methylheptene were formed. Employing 2-propanol as a reactant resulted in a product distribution containing aromatics including *p*-xylene and 1-ethyl-2-methylbenzene and olefins including 3-methyl-2-hexene and 3-methyl-2-pentene. Of all the butanols reacted over H⁺-ZSM-5, only 2-methyl-2-propanol (*tert*-butanol) gave the most significant aromatic yield. The remaining butanol isomers mainly gave branched alkanes and alkenes (Li et al., 2001).

Solid acid catalysts have been widely used and are industrially important because of the hydrocarbon isomerization process (Nel and de Klerk, 2007). Zeolites are also used as a catalyst for the isomerization process (Kriz et al., 1998). γ -Alumina also showed good activity on the reconstruction of straight chain hydrocarbons to branched, cyclic, and aromatic compounds (Sotelo-Boyas et al., 2011).

Hydrotreating and/or the hydrocracking process usually follows the FTS process to upgrade these long chain paraffins to the desired range of ATFs or jet fuels. The designed catalyst contains these hydrotreating/hydrocracking functions. The Co–Mo/ γ -Alumina catalyst has been widely used as a hydrotreating/hydrocracking catalyst in the petroleum industry (Baumgarten et al., 1983). Supported Co–Mo catalysts have been used in the petroleum refining industry for the past half century due to their reliable activity and thermal resistance (Lamprecht, 2007). Co–Mo bimetallic nanocatalysts were found to enhance the CO conversion in FTS. Incorporation of Mo into Co nanocatalyst led to better reducibility and higher H₂-consumption which would have resulted in more metal active sites available for FTS. Thus, it enhanced catalytic activity compared to those of the monometallic nanocatalysts (Reddy et al., 1998).

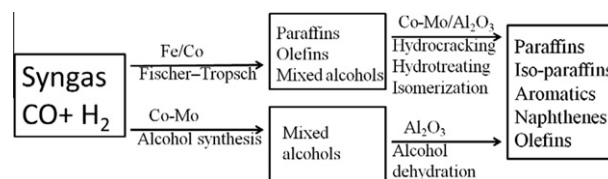
Promoters are also an important part of a catalyst. K₂O has shown a superior ability to improve the selectivity and stability of catalysts. It is an important promoter for both the FTS and CO hydrogenation catalysts, and therefore, K₂O was chosen as the promoter of the multifunctional catalyst used in this study.

Overall, the K–Fe–Co–Mo– γ -Alumina catalysts designed for this study were expected to be capable of converting syngas to jet fuel-range hydrocarbons in a single reaction step since they contain several catalytic functions. Scheme 1 illustrates the reactions and the selected active phases involved over the K–Fe–Co–Mo/ γ -Al₂O₃ catalyst. The bimetallic Co–Mo provides the active sites to convert CO into a mixture of alcohols from syngas. Iron and cobalt contain the hydrocarbon synthesis active sites for forming paraffins from syngas. γ -Al₂O₃ has the capability to dehydrate alcohols to paraffins, iso-paraffins, aromatics, naphthenes, and olefins. γ -Al₂O₃ also acts as the isomerization active components to restructure straight chain paraffins to branched paraffins and naphthenes. Co–Mo/Al₂O₃ is well known as a hydrotreating/hydrocracking catalyst to upgrade long chain paraffins to iso-paraffins, aromatics, and naphthenes. Alkaline metal K is the promoter to improve catalyst selectivity and stability.

3.2. Syngas production from wood chips

Many studies have been carried out to produce high quality syngas from natural gas or coal (Labrecque and Lavoie, 2011). In current work, syngas was generated from wood chips through gasification process. The composition of the producer gas was stable during gasification, which was monitored by a portable gas analyzer (7900P4C, NOVA Analytical Systems, Inc.). Fig. 1 showed the gas concentration variations during one run. The portable gas analyzer was not calibrated and was used only for monitoring the fluctuation of main gas concentrations. The gas concentrations measured by Agilent 6890 GC were used for material and energy balance analysis.

The syngas from the gasifier contained about 18% H₂, 21% CO, 12% CO₂, 2% CH₄ and 46% N₂. Besides of these main components, producer gas typically contains 500–3,000 ppm of tars, 0.5–2% oxygen, 200–1000 ppm of ammonia, and 200–400 ppm of sulfur components (H₂S and COS) [29]. After passing through the syngas cleaning unit, impurities in the producer gas were removed; the



Scheme 1. Illustration of the reactions of syngas to synthetic aviation turbine fuels over the K–Co–Mo– γ -Alumina catalyst.

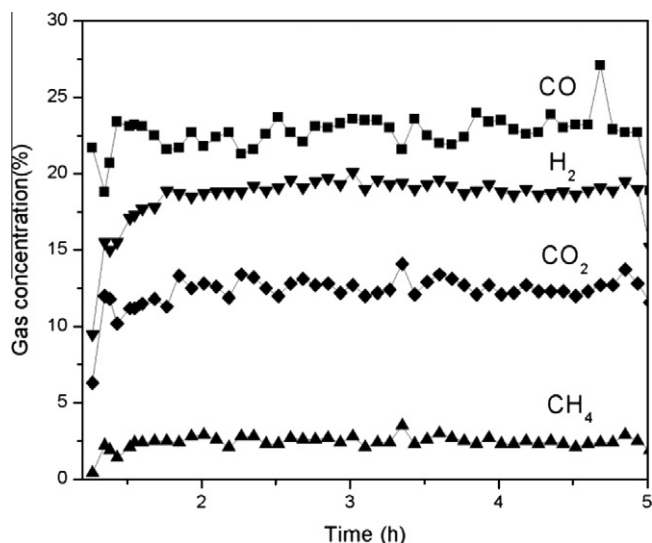


Fig. 1. Typical syngas composition monitored by a portable gas analyzer.

cleaned producer gas met the industrial requirements for catalytically converting the syngas ($\text{CO} + \text{H}_2$) to liquid fuels. The sulfur content ($\text{H}_2\text{S} + \text{COS}$) was less than 10 ppb, the ammonia content (NH_3) was less than 1 ppm, and the oxygen content (O_2) was less than 1 ppm (Yan and Yu, 2012).

3.3. Catalytic conversion wood syngas to liquid hydrocarbons

The influence of different operation parameters (catalyst bed temperature, reactor pressure, and GHSV) on the behavior of the

FTS process was studied. Producer gas passed through the single tube reactors and was converted to liquid hydrocarbons. The effluent flow was cooled and condensed, and then water was separated from oil phase. The CO conversion and hydrocarbon distribution were measured in a fixed bed flow reactor operating at a temperature of 250–350 °C, a gas hourly space velocity (GHSV) of 500–3000 h^{-1} , and a pressure of 3.14 to 8.62 MPa.

3.3.1. Effect of temperature

The temperatures studied were 250, 270, 290, 310, 330 and 350 °C, with the remaining conditions maintained constant. Three grams of catalyst were loaded into the reactor, and producer gas was fed into the reactor. The operating pressure was maintained at 6.89 MPa while the gas hourly space velocity was maintained at 3000 h^{-1} . The control of the reaction temperature is an extremely critical step since the FTS is a highly exothermic process, and high temperature may lead to the sintering of the catalyst, a decrease in the CO conversion rate, and a product selectivity shift to light hydrocarbons with increasing temperature.

Fig. 2 shows the CO conversion, the carbon dioxide and hydrocarbon selectivity, the gas phase hydrocarbon distribution (wt.%) and the liquid hydrocarbon distribution with temperature. CO conversion increased from 53.2% at 250 °C to 85.6% at 350 °C, and the hydrocarbon distribution also changed with temperature; the C_5^+ hydrocarbons decreased with increasing of temperatures from 66.5% at 250 °C to 57.4% at 350 °C. Fig. 2c shows the liquid fuel distribution in six groups, i.e., paraffins, iso-paraffins, aromatics, naphthenes, olefins, and oxygenates. Results indicate that paraffins decreased from 35.20% to 14.90% as the temperature elevated from 250 to 350 °C; iso-paraffins increased from 20.3% at 250 °C to 25.8% at 350 °C; olefins decreased from 21.3% at 250 °C to 14.2% at 350 °C; aromatics increased from 18.1% at 250 °C to 30.8% at

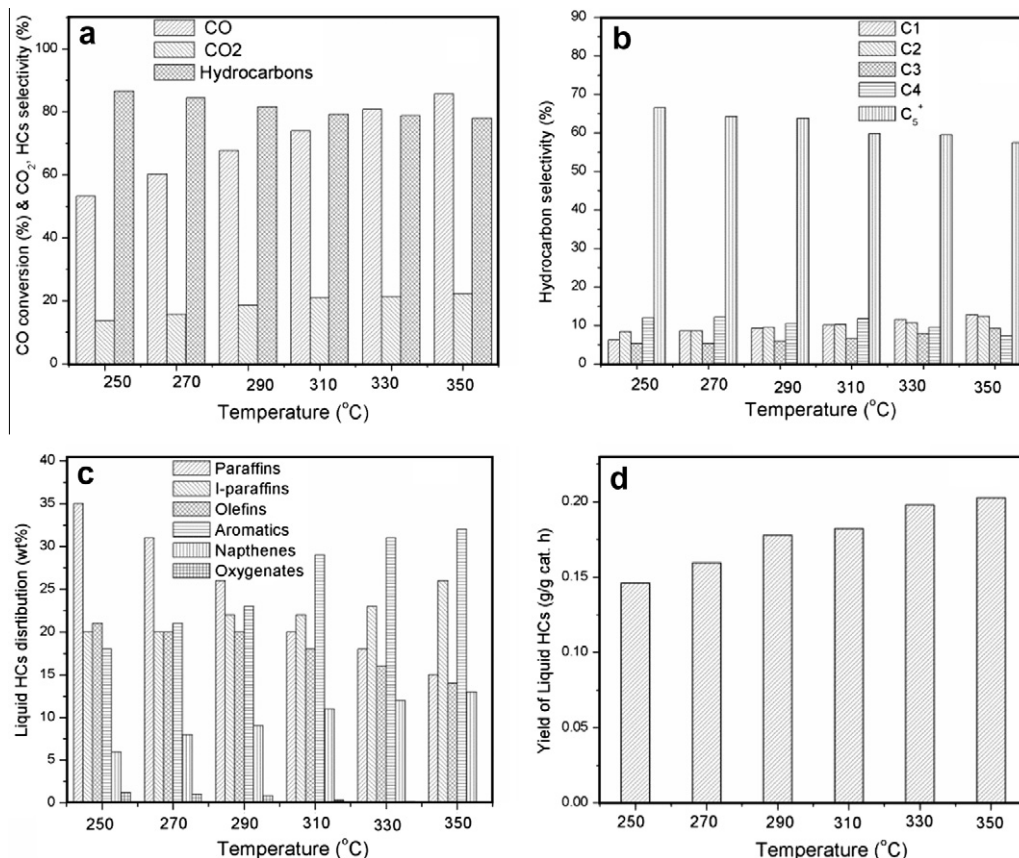


Fig. 2. Effect of temperature on (a) CO conversion, CO_2 and hydrocarbon selectivity, (b) hydrocarbon distribution, (c) liquid hydrocarbon distribution, and (d) yield of liquid hydrocarbons at 6.89 MPa, with wood syngas, GHSV of 3000 h^{-1} ; 3 g of catalyst was used in the reaction. Time on stream was 48–100 h.

350 °C; naphthenes increased from 6.3% to 12.8%; while oxygenates decreased from 1.21 to 0.03%. Fig. 2d illustrates the liquid fuel yield versus reaction temperature, the yield rate of the liquid hydrocarbons increased from 0.146 g/(g cat h) at 250 °C to 0.203 g/(g cat h) at 350 °C.

The results show that there is a balance between two trends: the CO hydrogenation reactions yielding alcohols, mainly due to the bimetallic Co–Mo, with an optimum temperature of 250–300 °C, and the acid function-based reactions, i.e., the conversion of oxygenates to hydrocarbons or aromatization, mainly due to the γ -Al₂O₃, with an optimum temperature of 300–350 °C. A compromise between these two trends leads to an optimum reaction temperature to give the maximum aromatics, iso-paraffins, and naphthenes yield. On the other hand, although the C₅⁺ fraction decreases in absolute terms, the aromatics, iso-paraffins, and naphthenes fractions increase relative to the total C₅⁺ fraction when the temperature increases above 300 °C, so that the liquid fraction becomes richer in aromatics, iso-paraffins, and naphthenes. It has been proven that increasing the operating temperature results in a shift in selectivity toward lower carbon number products and more hydrogenated products for all FT catalysts (Yan et al., 2008; Gujar et al., 2009). The degree of branching increases, and the amount of secondary products formed (such as ketones and aromatics) also increases as the temperature is raised. These shifts are in line with thermodynamic expectations and the relative stability of the products. As Co is a more active hydrogenating catalyst, the products are generally more hydrogenated, and the CH₄ selectivity rises more rapidly with increasing temperature.

3.3.2. Influence of pressure on the catalyst performance

An increase in total pressure will shift the equilibrium towards the product side of the reaction, and increase the CO conversion. Experiments under pressures of 3.45, 5.17, 6.89, and 8.62 MPa were conducted. Temperature was held constant at 310 °C, and the producer gas was employed as the feed gas. The space velocity was maintained at 3000 h^{−1}. The effect of pressure on both CO conversion and process selectivity showed that CO conversion increased with the increase of reaction pressure. Within the C₅⁺ fraction, an effect of pressure on selectivity was observed. The increase in pressure clearly favored the formation of C₅⁺, while C₁–C₃ gaseous hydrocarbons clearly decreased with an increase of the pressure. Fig. 3c shows the liquid fuel distribution in six groups. The results show that with the increasing of the reaction pressure, paraffins decreased from 25.7% to 19.5%; iso-paraffins increased from 18.3% to 23.0%; olefins decreased from 22.3% to 16.5%, aromatics increased from 21.6% to 31.5%; naphthenes were approximately unchanged and oxygenates increased from 0.21% to 1.56%. Fig. 3d shows the effect of pressure on the liquid fuel yield, the yield rate of the liquid hydrocarbons increased from 0.153 g/(g cat h) at 3.45 MPa to 0.230 g/(g cat h) at 8.62 MPa.

The effect of pressure on both CO conversion and process selectivity showed that when pressure increased, CO conversion increased. Within the C₅⁺ fraction, an effect of pressure on selectivity was observed. The increase in pressure slightly favored the formation of carbon molecules of the C₅⁺ range. The synthesis rates of both alcohols and hydrocarbons are dependent on the syngas pressure over the K–Fe–Co–Mo– γ -Alumina catalyst. Therefore, increasing syngas partial pressure results in an increased productivity of all

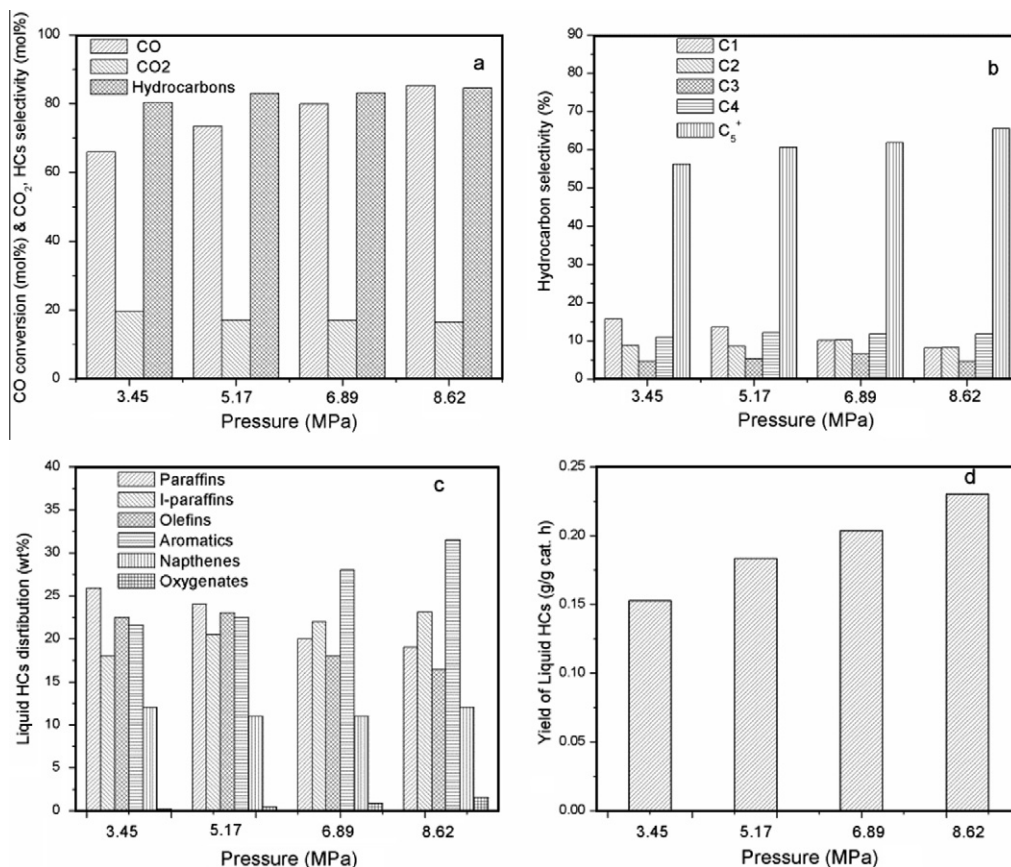


Fig. 3. Effect of pressure on (a) CO conversion, CO₂ and hydrocarbon selectivity, (b) hydrocarbon distribution, (c) liquid hydrocarbon distribution, and (d) yield of liquid hydrocarbons at 310 °C with wood syngas, GHSV of 3000 h^{−1}; 3 g of catalyst was used in the reaction. Time on stream was 48–100 h.

products with the exception of CO₂, which is not very sensitive to the change in syngas pressure. In the present study, a stoichiometric H₂/CO ratio of 1 seems to be an appropriate syngas composition for the synthesis of hydrocarbons.

The increase in pressure clearly favored the formation of C₅⁺, while C₁–C₃ gaseous hydrocarbons clearly decreased when the pressure was increased. Fig. 7c shows that when the reaction pressure was increased, the mole percentage of paraffins decreased from 25.7% to 19.5%, iso-paraffins increased from 18.3% to 23.0%, olefins decreased from 22.3% to 16.5%, aromatics increased from 21.6% to 31.5%, naphthenes remained relative, and oxygenates increased from 0.21% to 1.56%. Some previous FTS studies also showed that the product selectivity shifts to heavier products and more oxygenates (mainly alcohols) when the total pressure is increased (Li et al., 1998). More alcohols were generated under higher pressure, and more aromatics were formed since they are mainly formed from alcohol condensation over acid catalysts. Increasing pressure strongly affects performance of FT synthesis, and it was discovered that the type of reaction would change from FTS synthesis to hydroformylation when using cobalt catalysts as pressure increased (Iglesia, 1997).

3.3.3. Impact of space velocity on the catalyst performance

Experiments were completed with different GHSVs of 500, 1000, 2000, 2500 and 3000 h⁻¹. The remaining operating conditions of the producer gas were held constant at 310 °C and 6.89 MPa. The effect of the space velocity on CO conversion and hydrocarbon distribution showed that when the space velocity increased, CO conversion decreased as expected (Fig. 4). At the same time, C₅⁺ hydrocarbon production decreased. The effect of space time on product distribution was significant. It was observed that the yields

of hydrocarbons decreased with increasing space velocity. The gasoline fraction (C₅⁺) continuously decreased with increasing space velocity. Fig. 4c shows that with the increasing of the GHSV from 500 to 3000 h⁻¹, paraffins increased from 17.1% to 30.0%. Olefins decreased with the increasing of GHSV. Iso-paraffins, aromatics, and naphthenes were approximately unchanged, and oxygenates increased from 0.25% to 2.06%. Fig. 3d shows the effect of GHSV on the liquid fuel yield, the yield rate of the liquid hydrocarbons increased from 0.08 g/(g cat h) at 1000 h⁻¹ to 0.276 g/(g cat h) at 5000 h⁻¹. The increasing paraffin selectivity with increasing space velocity in this work may results from a decreased isomerization reaction and hydrotreating/hydrocracking rates for restructure straight chain paraffins to branched paraffins, aromatics, and naphthenes in the short contact time, while olefin selectivity decrease with decreased with increasing of GHSV may be due to less of alcohols condensed to olefins under high space velocity.

3.3.4. Time-on-stream performance

The time-on-stream effect on the performance of the K–Fe–Co–Mo–γ–alumina catalyst was studied at 310 °C over a period of 160 h. The evolution of CO conversion, light hydrocarbon and liquid product selectivity with time on stream are shown in Fig. 5. CO conversion was 78.3% at the beginning of the reaction and then decreased gradually to 72.5% after 160 h on stream. After 80 h on stream, no further change was observed over prolonged reaction times.

3.4. Analysis of liquid fuel from wood syngas

After the reaction, liquid hydrocarbon samples were collected from the condenser. The typical GC–MS spectrum shows the

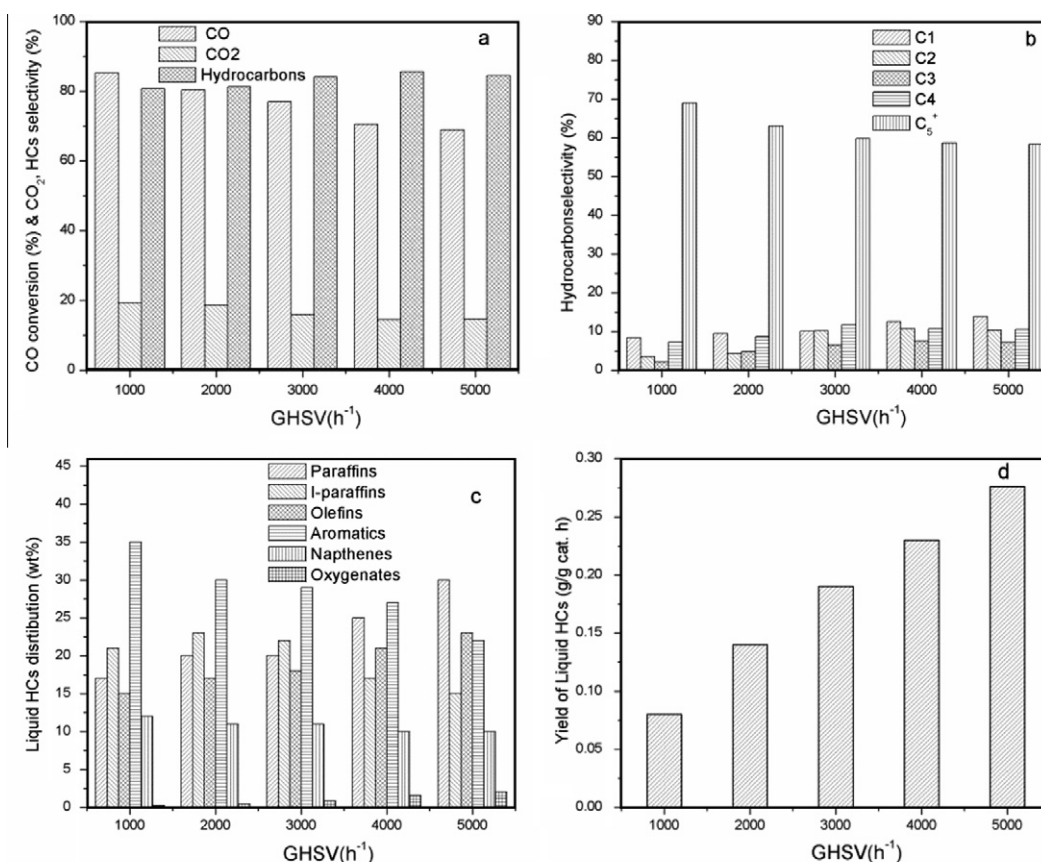


Fig. 4. Effect of GHSV on (a) CO conversion, CO₂ and hydrocarbon selectivity, (b) hydrocarbon distribution, (c) liquid hydrocarbon distribution and (d) yield of liquid hydrocarbons at 310 °C, 6.89 MPa with wood syngas; 3 g of catalyst was used in the reaction. Time on stream was 48–100 h.

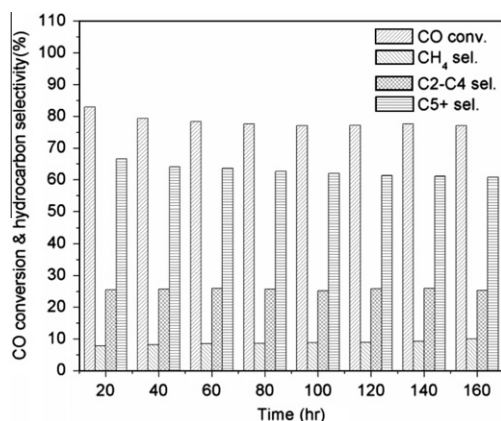


Fig. 5. Time on stream of CO conversion, hydrocarbon selectivity and distribution on the catalyst at 310 °C, 6.89 MPa, 3000 h⁻¹ with wood syngas.

product distribution can be separated into three zones, i.e., renitent time of 1.5 to 5.5 min, which includes C4–C8 products (olefins, iso-paraffins, paraffins, aromatics, naphthenes, and oxygenates). In the zone of 6.8–23.1 min, C8 (aromatics) and ~C19 hydrocarbons are located in this period of time, and the main products are aromatics, iso-paraffins, and naphthenes. The third zone is retention time between 24.3 and 37.4 min, and this zone includes products of C20–C26. These products are mainly long chain paraffins and iso-paraffins.

The liquid product characterization from the producer gas was performed by gas chromatography using the PIANO analysis. Liquid oil products were quantitatively reported in the volatile range up to molecules with 13 carbons with the five families of hydrocarbon groups (paraffins, iso-paraffins, aromatics, naphthenes, and olefins).

Table 1 shows typical liquid product fuels obtained with the catalyst. In general, it was observed that the main reaction products were olefins (totally about 25.33%) with a predominance of C7 (10.37%), C9 (5.07%), C6 (4.68%), and C13 (2.1%) components. The second largest group included aromatics, which contributed

19.84% (mol) from C7–C12 components with main components of C10 (13.78%), C12 (1.99%), C11 (1.91%), and C9 (1.55%). The largest amount of aromatic molecules include sec-butylbenzene (5.8211%), 1,2-dimethyl-3-ethylbenzene (4.7077%), 1,3-dimethyl-4-ethylbenzene (1.0227%), 1,2-ethyl-i-propylbenzene (0.5801%), 1,3-methyl-i-propylbenzene (0.5822%), 1,3-methylethylbenzene (0.5224%), and 1,3-dimethylbenzene (0.5935%). Iso-paraffins contribute 15.02% overall, from C6–C13 components. Naphthenes and paraffins comprised 8.05% and 12.94% of the liquid product, respectively. There are also 19.74% unidentified components in the liquid product due to the limitation of the data base. If reporting the liquid hydrocarbons by carbon numbers, C9s and C10s contribute 23.0% and 23.01%, respectively. The other carbon numbers are made up of the following: C7s (15.92%), C8s (15.28%), C12s (5.96%), C6s (5.81%), C11s (5.49%), C13s (5.13%), and C5s (0.74%). C8–C13 hydrocarbons contribute 77.87% of the liquid product. Besides hydrocarbons, there are also 3.1% oxygenates found in the liquid oil phase. These oxygenates are iso-propanol, ethanol, and tert-butanol.

Since hydrocarbons in ATFs are mainly C8–C17, the syncrude from producer gas was distilled to remove both lighter hydrocarbons and wax components. The production sample was collected by distillation with a boiling point between 110 and 310 °C. The GC–MS spectrum shows that the distilled products were located in the retention time of 5.9–21.1 min. The C8 (aromatics) ~C17 hydrocarbons are found from this zone, and the main products were aromatics, iso-paraffins, paraffins and naphthenes.

Table 2 shows typical liquid products of the syncrude after distillation. In general, it was observed that the main products were aromatics (22.16%), iso-paraffins (19.63%), naphthenes (14.51%) and paraffins (14.11%). Most of the olefins have been removed (from 25.33% in the syncrude to 7.23%). This agrees with the GC–MS spectrum. By carbon numbers, C10s contribute 32.83%; followed by C9s (19%), C11s (13.14%), C12s (12.16%), C8s (9.15%), C13s (8.86%), and C7s (4.45%). C8–C13 hydrocarbons contribute 95.14% of the liquid product.

A commercial Jet A sample was also analyzed for comparative purposes. The DHA results of Jet A is listed in Table 4. The

Table 1

Typical product distribution of the C₅⁺ liquid fraction for the K–Fe–Co–Mo/γ-Al₂O₃ catalyst by group type and carbon number (in mol percent).

	Paraffins	Iso-paraffins	Olefins	Naphthenes	Aromatics	Unknowns	Total
C5	0.07	0	0.67	0	0	0	0.74
C6	1.1	0.025	4.68	0	0	0	5.81
C7	2.28	0.33	10.37	1.41	0.5	1.03	15.92
C8	2	0.79	1.26	1.5	0.61	9.12	15.28
C9	2.5	7.38	5.07	4.16	1.55	2.34	23
C10	2.92	4.23	0.5	0.77	13.78	0.81	23.01
C11	1.07	1.84	0.15	0.2	1.91	0.32	5.49
C12	0.503	0.41	0.032	0.012	1.99	3.01	5.96
C13	0.5	0.02	2.1	0	0	2.51	5.13
Total	12.94	15.02	25.33	8.05	19.84	19.74	81.18

Table 2

Typical product distribution of the C₅⁺ liquid fraction of the distillation by group type & carbon number (in mole percent).

	Paraffins	Iso-paraffins	Olefins	Naphthenes	Aromatics	Unknowns	Total
C5	0.03	0	0.02	0	0	0	0.05
C6	0.05	0.01	0.3	0	0	0	0.36
C7	1.3	0.1	0.88	0.92	0.95	0.3	4.45
C8	2.1	0.93	0.68	1.84	1.14	2.46	9.15
C9	1.52	2.8	2	5.46	2.04	5.18	19
C10	3.15	9.58	0.19	5.89	12.74	1.28	32.83
C11	2.59	4.06	0.36	0.4	2.96	2.77	13.14
C12	2.27	2.06	0.06	0	2.33	5.44	12.16
C13	1.1	0.09	2.74	0	0	4.93	8.86
Total	14.11	19.63	7.23	14.51	22.16	22.36	77.64

Table 3

DHA results of a commercial ATF (Jet A) sample.

	Paraffins	Iso-paraffins	Olefins	Naphthenes	Aromatics	Unknowns	Total
C5	0.01	0	0.01	0	0	0	0.02
C6	0.01	0	0.17	0	0	0	0.18
C7	1.01	0.1	0.48	0.64	0	0.01	2.24
C8	0.7	0.93	0.58	1.8	1.18	2.22	7.41
C9	2.3	7.11	0.78	5.9	2.05	1.34	19.48
C10	3	7.1	0.23	2.08	19.22	2.1	33.73
C11	2.58	3.65	0.39	0.77	3.02	4.31	14.72
C12	1.23	1.95	0.02	0	2.05	5.66	10.91
C13	2.11	1.1	0.96	0	0	7.33	11.5
Total	11.95	21.94	3.62	11.19	27.52	22.97	74.554

Table 4

Comparison of syncrude fuel from syngas, distilled fuels, and Jet Fuel JPA.

Properties	Syncrude	Distilled fuel	Jet fuel JPA
Average Molecular Weight (g/mol)	125.50	137.98	140.65
Relative Density (g/ml)	0.80	0.81	0.82
Reid Vapor Pressure @ 100 °F (37.8 °C) (psi)	0.55	0.16	0.04
Percent carbon	86.58	86.61	86.95
Percent hydrogen	13.29	13.36	13.05
Bromine number (Calc)	26.16	6.12	3.18
Total oxygen content (mass%)	0.1243	0.0252	0.0044
Freeze point (°C)	−28.5	−37	−40

GC–MS spectrum shows that the distilled products are located within the retention time of 5.9–23.2 min, and C8 (aromatics) ~C18 hydrocarbons are found within this zone. The main products are aromatics, iso-paraffins, paraffins and naphthenes.

Table 3 shows typical component distribution of a commercial Jet A fuel. The main components in Jet A are aromatics, iso-paraffins, paraffins and naphthenes. Aromatics contribute 27.52%, iso-paraffins contribute 21.94%, naphthenes contribute 11.19% and paraffins contribute 11.95%. There are also 3.62% of olefins in the commercial sample. By carbon numbers, C10s contribute 33.73% overall; followed by C9s (19.48%), C11s (14.72%), C12s (10.91%), C13s (11.5%), and C8s (7.41%). C8–C13 hydrocarbons contribute 97.75% of the liquid product.

The properties of syncrude fuel from producer gas, distilled fuels, and a commercial Jet A sample are listed in Table 4. Average molecular weights (g/mol) of these samples are 125.5 for the syncrude fuel from producer gas, 137.98 for the distilled syncrude, and 140.65 for the Jet A. The relative density of the Jet A sample is the highest in these three samples. The properties of the distilled sample are more similar to those of the Jet A sample. These results further demonstrate the successful synthesis of aviation turbine fuels from producer gas.

4. Conclusions

A continuous process including gasification, producer gas cleaning, and FTS was developed and evaluated to demonstrate BTL hydrocarbon fuel technology. Oak-tree wood chips were used as the raw materials, and they were first gasified to form producer gas (containing syngas) over a commercial pilot plant downdraft gasifier. A multi-functional K–Fe–Co–Mo– γ -Alumina catalyst was developed and tested to catalytically convert producer gas to synthetic aviation turbine fuels (SATFs). Liquid fuels were successfully synthesized from bio-syngas, and these fuels demonstrated similar properties which are relatable to commercial aviation turbine fuels (Jet A).

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