Synthesis of Carbon-encapsulated Iron Nanoparticles from Wood Derived Sugars by Hydrothermal Carbonization (HTC) and their Application to Convert Bio-syngas into Liquid Hydrocarbons

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Abstract

Carbon-encapsulated iron nanoparticles (CEIN) were prepared from a solution of Iron(II) chloride (FeCl_2) and wood derived sugars under hydrothermal carbonization (HTC) conditions. The obtained nanostructures were characterized by SEM, TEM, HRTEM, XRD, TPD, Raman, and FTIR. The size of these nano-spheres was approximately 100 to 150 nm in diameter with an iron core diameter of 10-25 nm. The carbon-encapsulated iron nanoparticles were used as catalysts to thermochemically convert wood derived syngas into liquid hydrocarbons. These nanoparticles showed excellent catalytic performance when used as catalysts for the Fischer-Tropsch synthesis (FTS) process, and these nanoparticles showed high selectivity towards creating C_5^+ hydrocarbons. While undergoing reactions with biomass derived syngas at 290 °C, the CO conversion rate from this catalyst was found to be 89.5 % and C_5^+ hydrocarbon selectivity was discovered to be 65 %.

Keywords: Carbon-encapsulated iron nanoparticles, Wood chips, Sugar, Wood syngas, Fischer-Tropsch synthesis

1 Introduction

Fischer-Tropsch synthesis (FTS) is a key step of biomass-to-liquid (BTL) technology to convert biomass into a wide range of liquid hydrocarbon fuels and highly valued chemicals[1-3]. Previous gas-to-liquid (GTL) technologies are mostly based on using high quality syngas (mainly pure CO and H₂). This type of syngas contains only small amounts of nitrogen. The downdraft gasifier used in this study (located at Mississippi State University) produced syngas from pine wood chips. The syngas from the gasifier contained about 47% N₂, 21 % CO, 18 % H₂, 12 % CO₂, and 2% CH₄[3]. Completely converting the H₂ and CO in this bio-syngas into liquid hydrocarbons without having to use a recycle loop is extremely desirable because of the high N₂ and CO₂ content. Therefore, it was important to develop highly active and stable catalysts for the best overall performance when thermochemically converting the bio-gas from the gasifier used in this study.

Many commercial FTS plants use cobalt-based catalysts, but the optimal H₂:CO ratio is approximately 1.8–2.1 for the most efficient conversion rates. Iron-based catalysts promote the water-gas-shift reaction and effectively convert syngas with lower H₂:CO ratios into highly valued products. This reactivity makes iron-based catalysts a good choice to convert synthesis gas derived from coal or biomass into fuels because both have relatively low H₂:CO ratios (usually less than 1). The particle size of the iron-based catalysts has been reported to significantly influence the FTS activity and selectivity[4]. Nano catalysts are of interest because nanosizing catalysts increase the surface area of the catalysts and expose more active sites so reactants can more readily interact with these sites. The use of nanosized metals could potentially enhance the activity of current heterogeneous catalysts that dominate the field of catalysis [5]. Nano-scaled iron catalysts are selected to catalytically convert syngas into liquid fuels due to their low H₂/CO usage ratio, high activity, and selectivity to more valuable olefins in

high temperature synthesis (HTFT). However, it is well known that low product selectivity, catalyst agglomeration, and sintering limit the use of the iron catalysts in high temperature operations [6]. There are several approaches to improving the long time stability of a metal-supported catalyst system, including generating a strong metal-support interaction (SMSI) between the metal and support [7] and encapsulating metal particles within the support[8, 9].

In recent years, carbon-encapsulated metal nanoparticles have been reported as a new type of nanostructured carbon material. The nanoparticles have a typical core-shell structure of metal cores surrounded by carbon shells. These nanoparticles have potential value-added applications in magnetic data storage, xerography, electronics, catalysis, and drug delivery [10]. These nanoparticles have unique magnetic and electrical properties with high thermal and chemical stabilities. Carbon-encapsulated metal nanoparticles have previously been synthesized by using several methods. These methods include high-temperature annealing [10], arc discharging or modified arc discharging[11], and chemical vapor deposition (CVD)[12]. The synthesis of carbon materials is usually accomplished under extreme conditions by using high voltages (used with the arc discharging method) and high temperatures. These processes are not easily controlled and result in low product yields. The abundant and low-cost carbon sources from biomass are an easily obtained raw carbon precursor for value-added carbonaceous nanoparticle production. However, limited study has been reported on the use of wood or agricultural biomass as the carbon source for these nanoparticles[13]. The carbon content of wood varies from about 47 to 53%. Therefore, it is very important to find a method to synthesize carbon-encapsulated metal nanoparticles using low-cost biomass carbon sources[14]. Hydrothermal carbonization processes have been considered for the conversion of biomass to produce fuels and other value-added products [15-17]. A sulfonated carbon material was

prepared by incomplete hydrothermal carbonization of glucose followed by sulfonation, and it exhibited high catalytic performance during the hydrolysis of cellulose[13].

In this study, highly functionalized carbon-encapsulated iron-core nanoparticles were synthesized by low temperature hydrothermal carbonization (HTC) using sugars derived from pine wood as precursors. The nanostructures obtained from this study were characterized by SEM, TEM, HRTEM, XRD, TPD, Raman, and FTIR. The possible mechanism of the HTC process from sugars was proposed according to the results of characterization and gas phase composition. The principal objective of this work was to develop a highly efficient carbon-encapsulated metal nanoparticle catalyst for FTS by using an alternative raw material. The activity, selectivity, stability, and life-time of the nano-catalyst were evaluated. The detailed hydrocarbon analysis (HDA) of the liquid produced from the bio-syngas was also performed.

2 Experimental

2.1 Sugars from pine wood

The southern pine wood chips (<10 mm in length) were used as the feedstock to produce sugars using an acid hydrolysis. The pine wood chips were first dried to a maximum moisture content of 10%. After drying the chips, they were treated with 72% H₂SO₄ (150 ml) at 30°C for 1 h to remove lignin. The treated pine chip solution was hydrolyzed by adding 4200 ml of water and using an autoclave to heat the solution to 121 °C for 1 h. The resulting hydrolysis solution was filtered through the crucibles with a filtering disc to separate the filtrate and residue. The filtrate was used to determine the contents of cellulose, hemicellulose and acid-soluble lignin, while the residue was used to determine acid-insoluble lignin. The filtrate was analyzed for glucose, xylose, arabinose, galactose and mannose by HPLC analysis. Conversion factors were used to convert monomer sugar concentrations into polymeric compositions found in the starting

materials. The acid-soluble lignin in the filtrate was determined by spectrophotometry. Lignocellulosic compositions including glucan, xylan, arabinan, galactan, mannan and lignin were determined by using the NREL method for “Determination of Structural Carbohydrates and Lignin in Biomass” [18].

2.2 Preparation of carbon-encapsulated iron-core nanoparticles

Carbon-encapsulated iron-core nanoparticles were synthesized hydrothermally by the reduction of Fe^{2+} in the sugar solution derived from pine wood. Ten grams of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in the 250 ml pine derived sugar solution (the pH value of the solution was 3.0). The mixture was stirred for 30 min then transferred into a one-liter Parr reactor. After the autoclave was sealed, the sample was heated and the temperature was maintained at 160 to 180 °C for 8 h [19]. After the reaction took place, a black product was obtained. The product was collected and washed three times with DI water and ethanol to remove soluble ions and sugar residues. The waste water containing sulfate acid was first neutralized with calcium carbonate then released to environment. The final product was oven-dried at 110 °C for 12 h. The dried carbon-encapsulated iron nanoparticles were loaded to a 2-inch tubular reactor and ramped at 2°C/min to 700 °C under a nitrogen flow (100mL/min) with a dwell time of 1 h. At this point, the sample was ready for testing in the catalytic conversion process. Twelve grams (12.0 g) of carbon-encapsulated iron nanoparticles were obtained after being calcined at 700 °C. Elemental analysis was performed using a PerkinElmer 2400 Elemental Analyzer (to determine the C, H and O content) and a PerkinElmer NexION 350 Inductively Coupled Plasma Mass Spectrometer (ICP-MS) was used to determine the iron content. The results showed that the sample contained 20.8 wt% iron (Fe), 71.7wt% carbon (C), 0.8wt% hydrogen (H), and 7.5wt% oxygen (O), respectively.

2.3 Catalytic reaction

The synthesis gas conversion reaction was carried out in a lab-scale continuous flow fixed-bed reactor system. Bio-syngas was generated through the gasification process using pine wood chips as the raw material. Bio-syngas preparation and cleaning has been discussed in our previous work [20]. Wood chip gasification was performed using a pilot-plant scale downdraft gasifier (BioMax 25). The producer gas was first compressed to approximately 0.31 MPa. A syngas pre-purification process was designed to remove the poisoning or negative components (e.g., moisture, sulfur, ammonia, tar and oxygen). The effluent producer gas contained approximately 46% N₂, 21% CO, 18% H₂, 13% CO₂, and 2% CH₄. The producer gas was finally compressed to approximately 13.8 MPa using a 2-stage pneumatic air pump obtained from Hydraulics International (Chatsworth, CA).

The Fischer-Tropsch synthesis reaction equipment used in this research was a fixed-bed reactor constructed out of 316 stainless steel (with a 12.7 mm inner diameter and a length of 0.61 m). Three grams of the calcined carbon-encapsulated iron nanoparticles were loaded into the reactor. A thermowell located at the center of the reactor allowed the placement of the thermocouples to monitor the temperature of the catalyst bed. The reactor was first purged with N₂ at a flow rate of 100 mL/min at room temperature for 30 min. Next, the catalyst was introduced to the bio-syngas at 400 °C for 8 h. the reactor was adjusted slowly to the desired temperature, and bio-syngas was fed into the reactor until reaching the desired pressure. The reaction was operated under the following conditions: a temperature range of 230 to 330 °C, a gas hourly space velocity (GHSV) of 2000 to 8,000 h⁻¹, and a pressure range of 3.45 to 8.62 MPa. The gas flow rate was metered using Brooks mass flow controllers. The product stream from the reactor passed through a gas-liquid separator, where the temperature was held at 0 °C. The gas

phase product from the condenser passed through a back pressure regulator and was separated into two streams. One stream passed through a wet-test flow meter. The other stream flowed into an on-line GC auto-sampling valve with a flow rate of 25 mL/min.

2.4 GC and GC/MS analyses of gas and liquid products

The details of the gas and liquid product analysis method are discussed in our previous work [18]. The analysis of gas phase products was carried out with an on-line Agilent 6890 gas chromatograph with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Liquid samples were analyzed using an Agilent 7683B Series Injector coupled to an Agilent 6890 Series gas chromatograph system, a 5973 Mass Selective Detector, and a FID detector. The detailed hydrocarbon analysis (DHA) of liquid hydrocarbons was performed over a Perkin Elmer Clarus 680 GC with a FID detector. The data obtained for each reaction condition were recorded three times, and the obtained average values were used as the experimental results. The standard deviations of the data were approximately zero. The conversion (X_{CO}) was defined as the CO converted per total amount of CO according to Eq. (1).

$$X_{CO}(\%) = \frac{C_{COin} - C_{COout}}{C_{COin}} \times 100 \quad (1)$$

C_{COin} is the initial molar fraction of CO in the feed, and C_{COout} is the final molar fraction of CO in the gaseous effluent.

The selectivity of CO_2 (S_{CO}) is defined according to Eq. (2).

$$S_{CO_2}(\%) = \frac{C_{CO_2out}}{C_{COin} - C_{COout}} \times 100 \quad (2)$$

C_{CO_2out} is the final molar fraction of CO_2 in the gaseous effluent.

The selectivity of hydrocarbon i was calculated according to Eq. (3),

$$S_i(\%) = \frac{n_{iout}}{C_{COin} - C_{COout}} \times 100 \quad (3)$$

C_i is the concentration of hydrocarbon component i in the effluent gas, and n is the carbon number in a product i .

2.5 Characterization

X-ray powder diffraction (XRD) patterns of the synthesized catalyst samples were obtained using a Rigaku Ultima III X-ray Diffraction System (Woodlands, TX). The system operated at 40 kV and 44 mA using Cu-K α radiation with a wavelength of 1.5406 Å. Angles of 15° to 80° were used at a scan rate of 0.02°s⁻¹. The sample morphology was investigated using Scanning Electron Microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX) (JEOL JSM-6500F, Peabody, MA). All samples were pre-coated with gold before being introduced into the vacuum chamber. The system was operated with an accelerating voltage of 5 kV. The sample particle sizes were examined with a JEOL JEM-100CX II (Peabody, MA). The Transmission Electron Microscope (TEM) operated at accelerating voltage of 100 kV. All samples were sonicated in an ethanol solution for 20 min before being transferred to the copper supports. Fourier transform infrared spectra (using a Nicolet 6700 FT-IR Spectrometer) characterized the functional groups on the samples. A Jobin–Yvon microspectrometer was used to investigate the Raman spectra on the samples with an excitation laser source emitting at 514 nm. An incident power of around 1 mW was used (on a thin surface of a few μm^2 covering dispersed samples). Thermogravimetric analysis (TGA) experiments were carried out with a Shimadzu TGA-50H (Columbia, MD) using isothermal analyses. The change in mass was then related to the changes taking place in the sample during calcination. Nitrogen (99.999% purity, 50 ml/min) flowed through the TGA at 50 ml/min as the temperature was ramped at a rate of 10 °C/min. Temperature-programmed desorption (TPD) experiments involved heating the carbon-encapsulated iron-core nanoparticles nanostructure in a purging gas at a programmed heating rate

(2 °C/min) to induce thermal desorption of the adsorbed species from the surface. Volatile species from the carbon-encapsulated iron-core nanoparticles were analyzed using an on-line Agilent 7890 GC during the TPD process. TPD experiments were carried out in a fixed-bed, 12.7 mm tubular stainless-steel reactor. A 5 g sample was used in each run. High purity nitrogen was used as the carrier gas with a flow rate of 20 ml/min.

3. Results and discussion

3.1 Hydrolysis solution from pine wood chips

The lignocellulosic composition of the hydrolysis solution included glucose, xylose, arabinose, galactose, mannose, and lignin. These components were determined by the NREL method[17]. Sugars like glucose, xylose, arabinose, galactose, and mannose formed after the pine wood hydrolysis from the H₂SO₄ acid pretreatments. The hydrolysis solution contained 33.3% glucose, 4.75% xylose, 1.42% arabinose, 2.90% galactose, and 15.4% mannose, respectively. There was also 41.6% lignin and 0.6% ash. All the above sugars (glucose, xylose, arabinose, galactose, and mannose) were important sources for the preparation of nano-carbon materials by using the HTC process. The results from a previous study[21] revealed a higher nano-carbon yield for xylose when compared to this study (80.2 g of nano-carbon spheres were obtained per 100 g of xylose). The previous study [21] also showed a lower nano-carbon yield that was observed for cellulose when compared with this study (28 g per 100 g cellulose). The differing nano-carbon yield is possible due to different carbonization tendencies of these sugars. Xylose begins to decompose at ~ 140 °C[22, 23] while the decomposition temperature of glucose, arabinose, galactose, and mannose is between 160 to 180 °C[24-26].

3.2 Gas phase composition after hydrothermal carbonization process

The mixture of the hydrolysis solution from pine wood chips and FeCl_2 was used to prepare carbon-encapsulated iron-core nanoparticles by using the hydrothermal carbonization (HTC) process. The reaction was performed in an autoclave at 180 °C for 8 h. The pressure of the reactor was increased gradually to 2.0 MPa at 180 °C during the HTC process. The final pressure was 0.54 MPa after the reactor cooled to room temperature. Some gaseous products were formed during the HTC process. Acid was still present in the sugar solution which catalyzed dehydration and hydrolysis. Formic acid and levulinic acid are possible intermediates and they contribute to gas production in the HTC process. The gaseous product from the reactor was analyzed using an Agilent 7890 GC, and the volume of the gaseous product was made up of 37.0% H_2 , 10.6% CO , 45.3% CO_2 , 0.05% C_2H_6 , 0.001% CH_4 , 0.01% C_3H_8 , and 3.8% N_2 . A trace amount of ethylene (less than 0.001%) was also identified by the on-line GC. A trace amount of benzene was previously detected using an on-line residue gas analyzer (RGA) from the gas phase of glucose, xylose, sucrose and cellulose after the product underwent HTC [21]. During the HTC process, sugars are dehydrated and hydrolyzed in the acidic solution. Water soluble molecules are formed by the saccharification process and then go through a second decomposition process where the elimination of the functional groups is carried out. This results in the formation of gaseous products and water insoluble products. Next, the aromatization occurs from these products [12]. The carbon formation of sugars takes place via: (i) dehydration and fragmentation of sugars; (ii) polymerization or condensation of the dehydrated and fragmented products; (iii) aromatization of the polymers; and (iv) nucleation and subsequent growth by diffusion and linkage of species from the solution to the nuclei surface [13, 15].

3.3 Characterization of carbon-encapsulated iron-core nanoparticles

Figure 1 shows the XRD patterns of the fresh carbon-encapsulated iron nanoparticles. Carbon-encapsulated iron nanoparticles were synthesized hydrothermally by the reduction of Fe^{2+} in a pine wood derived sugar solution. Next, the carbon-encapsulated iron nanoparticles were calcined under a nitrogen flow at 700 °C, and then the calcined carbon-encapsulated iron nanoparticles were used in the catalytic conversion process. There were negligible diffraction peaks observed for the fresh sample (Fig. 1a), which indicates that both the core and the shell are in an amorphous structure.

The pattern of the sample calcined under a N_2 flow at 700 °C (Fig. 1b) showed one peak at 44.68 ° that corresponded to the α -iron (110) plane (PDF#97-005-3802). The peaks 37.75 °, 40.7 °, 42.6 °, 43.75 °, 44.56 °, 44.94 °, 45.86 °, 49.12 °, and 57.8 ° are assigned to cementite, Fe_3C with correspondence planes of (121), (210), (201), (211), (102), (220), (031), (112), and (221), respectively (PDF#00-035-0772). The pattern of the post-reacted carbon-encapsulated iron nanoparticles (after being used in the catalytic conversion process) was similar to the calcined one (Fig. 1c). There is no peak at 26.55 ° which corresponds to carbon (002) plane observed for all samples, and this shows that the carbonaceous shell was not modified with the addition of graphite after the calcination at 700 °C or the FTS process. This also shows that it still exists as an amorphous state. The existence of α -iron and Fe_3C confirms that both metal iron and iron carbide are the active phase of the catalyst during bio-syngas catalytic conversion.

SEM images of the carbon-encapsulated iron-core nanoparticles are shown in Fig. 2. The core-shell structure is spherical in shape. Spherically shaped particles with a uniform particle size were observed for the product. The morphology of the single micro-sphere exhibits a porous structure surface. The diameters of the fresh core-shell structure were between 100 and 200 nm. The SEM image of the calcined carbon nano-spheres at 700 °C shows the particle size is almost

uniform at 50 - 100 nm. These calcined nano-carbon spheres showed more uniform distribution compared to the fresh ones.

The TEM images of carbon-encapsulated iron-core nanoparticles are shown in Fig.3. The TEM image of the fresh core-shell catalyst shows that the diameter of core-shell was about 100 - 200 nm (Fig. 2a). The diameter of the iron core structure was between 15 to 25 nm. The TEM image of the calcined carbon nano-spheres (after being heated to 700 °C) showed the particle size to be 50 nm (Fig. 2b). The diameter of the iron core structure of the calcined non-sphere was between 10 and 20 nm. Carbon-encapsulated iron-core nanoparticles shrank due to the decomposition of the functional groups of the carbonaceous shell and the reduction of iron oxide during the calcination process. HRTEM images of carbon nano-spheres from pine wood derived sugars derived by HTC at 180 °C are shown in Figs.3d and 3e. HRTEM images of carbon nano-spheres show that the diameter of the core nano-spheres were approximately 10 - 20 nm. The carbon shell exhibited a porous structure and was an amorphous structure since no ordered planes of the natural graphite structure were observed.

The Raman spectrum has the ability to identify the presence of the graphite and disordered amorphous carbon in the samples. The Raman spectrum obtained for the core-shell nanostructures is presented in Fig. 4. A peak at 1610 cm^{-1} was clearly seen in the Raman spectra of the fresh nanostructures, while a higher background of the fresh sample was also observed which is attributed to the high photoluminescence properties of the core nano iron particles[27]. The Raman spectrum of the calcined sample was also obtained. The calcined sample was thermally treated at 700 °C with a heating rate of 2 °C/min in a N₂ atmosphere for 1 h. There were two peaks around 1587 and 1366 cm^{-1} , respectively. These peaks are attributed to the stretching modes of C–C bonds of the G band (in-plane vibrations of graphitic carbon) and D

band (disorder-induced band due to double-resonance effect) in the carbonaceous solid, respectively. Raman spectra also revealed the presence of C sp² atoms in benzene or condensed benzene rings of amorphous (partially hydrogenated) carbon [28]. This shows that small aromatic clusters were present in the core-shell samples. The difference found in the two spectra means that thermal treatment promotes the carbonization of the carbonaceous shell of the nanostructures.

The FTIR spectrum obtained for the fresh core-shell nanostructures is also presented in Fig.4. There are several bands which reveal that aromatization processes take place during hydrothermal carbonization (HTC). The characteristic vibration peaks of benzene framework positioned at 1605 and 1510 cm⁻¹ indicate the existence of a benzene ring structure in the carbonaceous shell, which confirms the idea of aromatization of sugar during hydrothermal treatment [29]. The presence of aromatic rings was also shown by the band at 1620 cm⁻¹ (attributing to C-C vibrations) and the bands in the 875 - 750 cm⁻¹ region (due to aromatic C-H out-of-plane bending vibrations). The vibration band at 1710 cm⁻¹ was attributed to the C=O vibrations of carboxylic acids, carboxylic anhydrides and lactones. The band at 3000 - 4000 cm⁻¹ was assigned to the -OH stretching vibrations, which implied the existence of hydroxyl groups. The band at 2980 cm⁻¹ corresponds to the stretching vibrations of aliphatic C-H and shows that the carbonaceous shell also possesses aliphatic structures.

The IR technique has been widely used to study changes in carbon surfaces after being heat treated. A decrease in the intensity of the characteristic IR bands reflects a change in the surface chemistry upon decomposition of the surface functional groups during thermal heating of carbon-based materials. The infrared bands associated with oxygen containing surface groups disappear or decrease in intensity after the sample is calcined at 700 °C for 1 h. The decrease in

the intensity of the bands at 1000 - 1450 cm^{-1} and 3000 - 3700 cm^{-1} (when comparing the fresh sample to the calcined sample) suggests that dehydration occurred during the thermal treatment of the carbon-encapsulated iron-core nanostructures and carbonization of the carbonaceous shell continued. The decrease of the intensity in the band at 1710 cm^{-1} is associated with the decomposition of carboxylic anhydrides and lactones which contain C=O groups. After the sample was heated, the weakened band at 1710 cm^{-1} indicated that most of these functional groups were removed. The peak at the 875 - 750 cm^{-1} region revealed aromatic C-H out-of-plane bending vibrations and showed similar behavior compared to the peak at 1710 cm^{-1} . This is explained in terms of internal structural reorganizations of aromatic structures and the acceleration of the carbonization of the shell during heat treatment at higher temperatures. The peak at 1605 cm^{-1} occurred because of the reorganizations of aromatic structures during carbonization, and the benzene framework showed the opposite behavior when compared to the peak at 1710 cm^{-1} . The band of 2980 cm^{-1} corresponded to the vibrations of C-H groups of saturated alkyl hydrocarbons and was unchanged after the sample was calcined. This was because the C-H group cannot be broken until reaching a temperature higher than 800 °C.

TPD analysis and on-line GC analysis were conducted to determine the gases that were produced during the calcination of the carbon-encapsulated iron-core structures. The surface functional groups that were chemically bound to the carbonaceous shell decomposed after being heat treated by releasing a plethora of gaseous compounds at different temperatures. The thermal desorption profiles provided useful information on the types of species desorbed from the shell surface and the interactions of the gaseous species with carbon. The amounts of these different surface groups were estimated by using the TPD spectra. Fig. 5a shows a typical profile recording the evolution of six species in gas phase: H_2 , CH_4 , CO , C_2H_6 , C_3H_8 , and CO_2 . Oxygen-containing

functional groups decomposed mostly as CO and CO₂[30]. Surface complexes yielding CO₂ groups decompose at two different temperatures and correspond to two types of functional groups[31]. Carboxylic acids ($\text{—COOH} \rightarrow \text{CO}_2$) are responsible for the low-temperature peak (100-400 °C)[31, 32], and the high-temperature CO₂desorption is attributed to carboxylic anhydrides and lactones (400-700 °C)[32, 33]. The CO-desorption groups are represented by three distinct groups of peaks. The peak temperatures of CO desorption centered at 400 °C correspond to the anhydride groups[33]. The CO peak centered at 500°C was probably due to the ether decomposition, and the CO peak at the temperature above 550 °C is contributed to the phenols and quinones[33]. The methane peak at 500 °C probably originated from the decomposition of the methyl group attached to aromatic units. Hydrogen on the carbon surface is found as chemisorbed water or as surface functional groups(e.g.carboxylic acids, phenolic groups)[32]. Hydrogen can also be bonded directly to carbon atoms as a part of aromatic or aliphatic structures. The C-H bond is very stable and breaks at approximately 800 °C without having to have a catalyst to break this bond. However, the desorption of hydrogen does happen at temperatures below 400 °C when transitional metals like iron, nickel and cobalt are used as catalysts to break down the C-H bond. Heat treatment in an inert atmosphere eliminates part of the hydrogen via surface reduction. The carbonaceous shell contains many oxygen-containing aromatic heterocyclic structures which decompose with the formation of carbon monoxide, methane and other low hydrocarbons. The interpretation of TPD spectra can be ambiguous to a certain degree because the temperatures of the desorption of molecules depend on the sample properties, the oxidation conditions, the probability of secondary reactions and the TPD conditions such as the heating rate[34].

Thermoanalytic techniques have been widely used to study the thermal behavior of biomass. The thermal decomposition of carbon-encapsulated, iron-core spheres was analyzed using TGA in N₂. The TG and DTG curves for the core-shell spheres between room temperature and 700 °C in N₂ atmosphere are shown in Fig.5b. TGA was used to determine the mass loss of the sample. The analysis was performed at 10 °C/min in nitrogen and normalized over the initial mass and the DTG/mass-loss rate was plotted with the increase in temperature. A continuous mass loss with increasing temperature was observed which shows the breaking of chemical linkages and the removal of volatile products from the sample. There are three possible steps of mass loss that are shown in Figure 8. The initial mass loss corresponds to the loss of physically adsorbed water. This loss occurs between ambient temperature and 130 °C with a peak temperature of 70 °C. After this loss occurs, it is followed by a steady rate of mass loss from 130 to 200 °C. The large loss of mass is observed around 200 to 700 °C and corresponds to the decomposition of all the functional groups in the carbonaceous shell. These results indicate that oxygen functional groups start to release in this temperature zone and lead to the initial aromatization of the char matrix. The maximum mass lost from the char is in the temperature zone of 350 to 700°C. This mass loss step primarily corresponds to the decomposition of the rest of the carboxylic anhydrides, lactones and part of the phenols, quinones, and ethers. They release the following volatile products: CO₂, CO, CH₄, H₂O, and H₂ (Fig. 5a).

3.4 Possible mechanism of sugar carbonization and formation of carbon-encapsulated iron-core nanoparticles under HTC process

The carbonization of sugar and the formation of carbon-encapsulated iron nanoparticles are very complex. When an aqueous sugar solution is hydrothermally treated at temperatures of 180 °C or greater, the sugar molecules hydrolyze with the catalytic promotion of iron ions which lead to

366 small carbonaceous colloids with a low degree of polymerization. Meanwhile, iron ions are also
367 hydrolyzed to FeOOH under the hydrothermal conditions [35]. Then, both polymerization and
368 condensation processes lead to the formation of insoluble polymers. Polymerization and
369 condensation reactions may be induced by intermolecular dehydration, dehydrogenation or aldol
370 condensation [36]. CO and hydrogen will also be released in this process (Section 3.2 and Fig.
371 5a). FeOOH will continue to be condensed and be further reduced to Fe_xO_y because CO and H_2
372 are released from the sugar carbonization process (Fig. 1). The Fe_xO_y nanoparticles then combine
373 with small carbonaceous colloids through Coulombic interactions with the surface functional
374 groups (e.g. OH and C=O) and condense to form Fe_xO_y -in-C nanorods [37]. These Fe_xO_y -in-C
375 nanorods are further assembled into Fe_xO_y @C core/shell nanospheres via further intermolecular
376 dehydration of the surface functional groups [38]. Fig.6 shows the TEM image of the one-hour
377 HTC sample. It displays numerous of needle-like nanorods in the early stage of the HTC process
378 and confirms the formation of Fe_xO_y nanoparticles. Fig.6 also shows the combination of the
379 Fe_xO_y nanoparticles with carbonaceous colloids from sugar carbonization. The Fe_xO_y
380 nanoparticles further catalytically promote the condensation and aromatization of carbonaceous
381 colloids around it. Aromatic clusters may be produced by the condensation of the aromatized
382 molecules generated in the decomposition/dehydration of the oligosaccharides or
383 monosaccharides [38]. Raman and FTIR results (Fig.4) reveal that aromatization processes take
384 place during hydrothermal carbonization (HTC). The characteristic vibration peaks of the
385 benzene framework indicate the existence of a benzene ring structure in the carbonaceous shell,
386 which confirms the aromatization of the sugar during the hydrothermal treatment [21]. The
387 presence of aromatic rings is also shown by the bands of the C-C vibrations (Fig. 4) and the
388 aromatic C-H out-of-plane bending vibrations. Previous work also has proven the presence of

benzene in the gas phase after the HTC reaction using a residue gas analyzer (RGA) [21]. When the concentration of aromatic clusters reaches the critical super saturation point, the formation of carbon nuclei takes place [39]. The formed nuclei of carbon grow by the diffusing of the chemical species present in the solution towards the surface of the Fe_xO_y nanoparticle [40]. These species are linked to the surface of the microspheres via the reactive surface functional groups (hydroxyl, carbonyl, carboxylic, etc.) present in the particles. The FTIR results show C=O vibrations of carboxylic acids, carboxylic anhydrides and lactones. The FTIR results also show –OH stretching vibrations which imply the existence of hydroxyl groups (Fig. 4). TPD spectra (Fig. 5a) of the carbon-encapsulated iron-core nanoparticles (after undergoing the HTC process in this study) showed the surface functional groups (hydroxyl, carbonyl, carboxylic, etc.) in these nano-carbon spheres. Stable surface functional groups such as ether and quinone were also formed.

Based on the above discussion and the characterization results of the catalysts, a possible mechanism of the formation process of the carbon-encapsulated iron-core nanoparticles is proposed. The mechanism is comprised of three steps. In the first step, sugar molecules are hydrolyzed with the catalytic promotion of iron ions when the aqueous sugar solution is hydrothermally treated at 180 °C. In the second step, reactions consisting of polymerization and condensation processes lead to the formation of insoluble polymers. The Fe_xO_y nanoparticles combined with small carbonaceous colloids and used the surface functional groups to condense and form Fe_xO_y -in-C nanorods. Finally, these Fe_xO_y -in-C nanorods were further assembled to Fe_xO_y @C core/shell nano-spheres via further intermolecular dehydration of the surface functional groups. Stable surface functional groups such as ether or quinone were also formed. Once the growth process stopped, nano-carbon shells over nano Fe_xO_y particles were completed.

3.5 Carbon-encapsulated iron nanoparticles as a catalyst for Fischer–Tropsch synthesis

Carbon-encapsulated iron-core nanoparticles synthesized by the hydrothermal process were used as a FTS catalyst. The CO conversion and hydrocarbon distribution were measured in a fixed bed flow reactor which operated at a temperature of 230 to 330 °C, a gas hourly space velocity (GHSV) of 2000 to 8000 h⁻¹ and a pressure ranging from 3.45 to 8.62 MPa.

The effect of temperature on the catalyst was established by varying the temperature and keeping other conditions constant. Temperatures of 230, 250, 270, 290, 310 and 330 °C were used. The operating pressure was kept at a constant pressure of 6.89 MPa, and the gas hourly space velocity was maintained at 4000 h⁻¹. Five grams of catalyst were loaded into the reactor. Bio-syngas from the gasifier produced from pine chips was used as the feed gas. Table 1 shows the CO conversion, carbon dioxide selectivity, hydrocarbon selectivity, gas phase hydrocarbon distribution (wt%), liquid hydrocarbon distribution and olefin distribution as the temperature was varied. CO conversion increased from 53.7% at 230 °C to 92.2% at 330 °C. The hydrocarbon distribution also changed with temperature. Light hydrocarbons (C₁-C₄) were favored at higher temperatures, and selectivity increased from 34.7% at 230 °C to 47.1% at 330 °C. Higher hydrocarbons were more sensitive to temperature change and underwent cracking and de-alkylation reactions that became more prominent with increasing temperature. Table 1 also shows the liquid fuel distribution: paraffins, iso-paraffins, aromatics, naphthenes (cycloalkanes), olefins, and oxygenates. Results indicate that as the temperature increased from 230 to 330 °C, paraffins decreased from 17.50% to 3.53%. Iso-paraffins first increased from 8.40% at 230 °C to 11.84% at 290 °C and then decreased to 10.87 % at 330 °C. Olefins increased from 36.6% at 230 °C to 48.90% at 290 °C and then decreased to 46.6% at 330 °C. Aromatics increased from 5.72% at 230 °C to 7.89% at 330 °C.

Olefins in the liquid fuels were analyzed and C₇, C₆, and C₅ were the main components. Table 1 shows the liquid olefin distribution between C₄ and C₁₃. The effect of temperature on olefin distribution was complex. There was no significant trend of the olefin selectivity with temperature.

An increase in total pressure shifted the equilibrium towards the product side of the reaction and increased the CO conversion. Experiments under pressures of 3.45, 5.17, 6.89, and 8.62 MPa were conducted. Temperature was held constant at 270 °C, and the bio-syngas was used as the feed gas. The GHSV was maintained at 4000 h⁻¹. Both the CO conversion and selectivity to C₅₊ hydrocarbons increased as pressure increased.

Table 2 shows that the CO conversion increased from 83.7% to 92.3% as the pressure was increased from 3.45 psig to 8.62 MPa. The increase in pressure clearly favored the formation of C₅₊ hydrocarbons, while the C₁~C₃ gaseous hydrocarbons remarkably decreased with an increase in pressure. Table 2 shows that as the reaction pressure increased, the production of paraffins, iso-paraffins, aromatics, naphthenes and olefins were all created at a consistent rate. However, the oxygenate selectivity increased from 2.9% to 6.5% as the pressure was increased from 3.45 psig to 8.62 MPa. The olefin selectivity shifted to heavier products as pressure was increased (Table 2). C₄ and C₅ hydrocarbon production decreased as pressure increased, while the production of C₇₊ olefins increased with increasing pressure, and C₆ olefin production remained unchanged.

Another set of experiments were completed by varying the GHSV. The following GHSVs were used: 2000, 4000, and 8000 h⁻¹. The temperature and pressure were held constant at 270°C and 6.89 MPa. The effect of the space velocity on CO conversion and hydrocarbon distribution showed that as the space velocity increased, CO conversion decreased (Table 3).

Table 3 shows that as the GHSV was increased from 2000 to 8000 h⁻¹, the C₅₊ hydrocarbon production decreased, and the CO conversion decreased from 89.2% to 72.93%. The effect of space time on product distribution was significant. The yield of hydrocarbons decreased as space velocity increased. The liquid fraction (C₅₊hydrocarbons) continuously decreased with increasing space velocity. Table 3 shows that after the GHSV was increased, paraffin selectivity increased from 3.56% to 9.90%, and oxygenate selectivity increased from 2.8% to 6.6%. Olefin production decreased after the GHSV was increased, and iso-paraffin, aromatic, and naphthene production remained constant. The olefin selectivity shifted to lighter products after increasing the GHSV (Table 3).

The time-on-stream effect on the performance of the carbon-encapsulated iron-core nanoparticles was studied at a temperature of 270 °C over a period of 160 h. CO conversion was 87.8% at the beginning of the reaction and then decreased gradually to 82.5% at 100 h on stream. After 100 h on stream, no further change was observed over the prolonged reaction time.

3.6 Properties and detailed liquid hydrocarbon distributions

The liquid products from bio-syngas were collected, and analysis of the products was performed by using a gas chromatography analysis. Liquid oil products were quantitatively reported in the volatile range with molecules containing up to 13 carbons of five families of hydrocarbon groups: paraffins, isoparaffins, aromatics, naphthenes (cycloalkanes), and olefins (PIANO). Oxygenates were also analyzed. Table 4 shows the typical liquid product fuels obtained after using the carbon-encapsulated iron nanoparticles as a catalyst.

In general it was observed that the main reaction products were olefins (approximately 49.11wt%) with predominance of C₅ (11.79%), C₆ (16.51%), C₇ (17.62%), and C₉ (1.97%) components. The richest alkenes found in the sample were 3,3-dimethyl-1-butene (1.70%), 2,3-

dimethyl-1-butene (2.18%), 2-methyl-1,4-pentadiene (1.50%), 1,4-hexadiene (6.11%), c-3-hexene (2.05%), 4-methyl-2-hexene (1.66%), 1,6-heptadiene (1.85%), t-3-heptene (6.95%), and 3-methyl-c-2-hexene (1.2%).

The second most prominent group found in the product was iso-paraffins, which contributed to 11.82wt% of the product. The main components were classified as C₅ (0.7 %), C₇(1.3%), C₈ (1.42%), C₉ (4.65%), C₁₀ (2.4%), and C₁₁ (1.15%). The predominate iso-paraffins in the liquid product included 2,2,3-trimethylpentane, 2,5-dimethylhexane, 2,3,4-trimethylpentane, 2-methylheptane, 2,2,5-trimethylhexane, 2,4-dimethylheptane, 4-ethylheptane, 3-methyl-5-ethylheptane, 2,3-dimethyloctane, and 3-ethyloctane.

Aromatics contributed 7.83wt% of the overall product and contained C₈~C₁₂ components which included sec-butylbenzene, 1,3-dimethylbenzene, 1,2-dimethyl-3-ethylbenzene, 1,2-di-i-propylbenzene, and 1,4-di-i-propylbenzene. Napthenes and paraffins comprised 5.4wt% and 5.1wt% of the liquid product, respectively.

There were also 10.74 mole% of unidentified components in the liquid product due to the limitation of the database. According to carbon numbers, C₇ hydrocarbons contributed the most (21.22%), followed by C₆ (18.93%), C₅(16.24%), C₈ (11.04%), C₉ (10.79%), C₁₀ (9.19%), C₁₁ (4.74%), C₁₂ (3.37%), and C₁₃ (2.27%) hydrocarbons. There were also 3wt% of oxygenates found in the liquid oil phase. These oxygenates included iso-propanol, ethanol, t-butanol and methanol.

3.7Catalytic performance of carbon-encapsulated iron nanoparticle catalysts

Tables 1-3 show the FTS results over the reduced carbon-encapsulated iron-core nanoparticles. The CO conversion was about 90% and C₅⁺ hydrocarbon selectivity reached a maximum of 65 % at 330 °C. Olefins contributed to approximately 50 % of the liquid fuels. The

time-on-stream effect on the performance of carbon-encapsulated iron-core nanoparticles showed that the CO conversion remained constant at 82.5 % after running 160 h. The carbon-encapsulated iron nanocomposite core-shell catalysts showed highly stable activity for the catalytic conversion of bio-syngas. DHA analysis of liquid hydrocarbons showed that following amounts of hydrocarbons were present in the product (mole%): 21.22% of C₇, 18.93% of C₆, 16.24% of C₅, 11.04% of C₈, 10.79% of C₉, 9.19% of C₁₀, 4.74% of C₁₁, 3.37% of C₁₂, and 2.27% of C₁₃ hydrocarbons. The ASF plot was plotted for the liquid fraction data to examine the product distribution over carbon-encapsulated iron-core nanoparticles. The ASF plot showed a nearly linear distribution in the C₅–C₁₃ region. The slope $\ln(\alpha)$ of the linear fitting result was -0.389. The chain growth probability α over carbon-encapsulated iron-core nanoparticles was calculated to be 0.68. This indicates that the step-wise mechanism is predominant, and the carbon-encapsulated iron-core nanoparticles showed a higher selectivity to produce liquid hydrocarbon products. In particular, the C₅₊ hydrocarbon fraction amounted to 60 mole% in the products, and this is higher than the values reported to date for iron catalysts without promotion. These catalysts include the Fe-*in*-CNT, Fe-*out*-CNT, and Fe/activated carbon catalysts [41, 42]. The high liquid product selectivity is contributed to the formation of nano ferrite (α -Fe), cementite (Fe₃C) in the nanocomposites after the catalyst underwent high temperature pretreatment conditions. TEM images (Fig.3) illustrate the fact that the carbon-encapsulated iron-core nanoparticles shrank due to the decomposition of the functional groups of the carbonaceous shell and the reduction of iron oxide during calcination process. The diffraction peaks of α -iron and Fe₃C confirmed both the metal iron and iron carbide are the active phase of the catalyst during the bio-syngas catalytic conversion (Fig. 1). The particle size of the iron species inside the carbonaceous spheres was 10 to 25 nm (Figs. 3) as a result of the transformation of Fe_xO_y into

iron carbides (θ -Fe₃C and α -Fe)[43]. Moreover, further gasification of the carbonaceous matter during the activation process ensured better accessibility of the embedded iron species to the reactants[44].

4 Conclusions

Carbon-encapsulated iron-core nanoparticles were synthesized with a low temperature hydrothermal carbonization method using pine wood derived sugars. The sugar solution was prepared by hydrolyzing pine wood chips with 2.48% H₂SO₄ acid pretreatments. A single micro-sphere had a porous structure surface. The diameter of the fresh core-shell structure was between 100 to 200 nm, and the particle size of the calcined carbon nano-spheres at 700 °C was almost uniform at 50-100 nm with the iron core having a diameter of 10 to 25 nm. The carbon-encapsulated iron-core nanoparticles used in this study demonstrated high activity and excellent stability for catalytic conversion of bio-syngas(19 % H₂, 20 % CO, 12 % CO₂, 2 % CH₄ and 47 % N₂) to liquid fuels. The results have shown that the catalyst had a maximum CO conversion of 90 % and a maximum liquid hydrocarbon selectivity of 65%. The DHA results indicated the main reaction products were olefins (49.11 mol%), and the second most prominent group created from the FTS process was iso-paraffins(11.82 mol%). Aromatics contributed 7.83 mol% overall (from C₈~C₁₂ components). There were also 3.0 % alcohols found in the liquid oil phase. The catalytic activity remained constant until 160 h. Fe nanoparticles did not sinter in any of the conditions of bio-syngas FTS reactions. The metal Fe core also provided the strong support for outer carbon shell to prevent the collapse of shell. The iron/carbon catalyst synergically formed core-shell nanocomposites that showed distinctive catalytic performance under a wide range of conditions.

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1	Caption of tables
2	Table 1 Effect of temperature on CO conversion, hydrocarbon selectivity, hydrocarbon
3	distribution, and liquid hydrocarbon distribution.
4	Table 2 Effect of pressure on CO conversion, hydrocarbon selectivity, hydrocarbon distribution,
5	and liquid hydrocarbon distribution.
6	Table 3 Effect of gas hourly space velocity (GHSV) on CO conversion, hydrocarbon selectivity,
7	hydrocarbon distribution, and liquid hydrocarbon distribution.
8	Table 4 Typical product distribution of the C ₅ ⁺ liquid fraction for the carbon-encapsulated iron
9	nanoparticles by group type and carbon number (in mol percent).

Table 1 Effect of temperature on CO conversion, hydrocarbon selectivity, hydrocarbon distribution, and liquid hydrocarbon distribution.

Temperature (°C)		230	250	270	290	310	330
CO conversion (%)		53.7	56.9	79.7	85.6	89.3	92.2
CO ₂ selectivity (%)		6.30	7.40	7.80	8.00	8.80	9.70
Hydrocarbon selectivity (%)		93.7	92.6	92.2	92.0	91.2	90.3
CH ₄ sel. (%)		10.2	11.5	11.2	12.1	13.5	15.7
C ₂ -C ₄ sel. (%)		24.5	25.2	27.1	29.2	30.1	31.4
C ₅ + sel. (%)		65.3	63.3	61.7	58.7	56.4	52.9
Liquid fuel distribution (%)	Paraffins	17.50	14.80	11.70	5.15	4.80	3.53
	I-Paraffins	8.40	8.99	9.74	11.84	10.65	10.87
	Olefins	36.6	39.76	43.75	48.89	48.01	46.36
	Napthenes	5.31	5.75	5.63	5.37	6.13	6.56
	Aromatics	5.72	6.09	6.75	6.82	7.23	7.89
	Oxygenates	6.71	6.56	6.52	6.44	5.50	4.33
Liquid olefin distribution (%)	C ₄ ⁼	11.81	9.02	8.80	6.93	8.25	9.07
	C ₅ ⁼	15.30	16.91	17.80	20.00	19.90	21.20
	C ₆ ⁼	28.10	27.70	29.50	30.7	28.30	26.73
	C ₇ ⁼	34.40	36.72	36.30	35.80	35.2	33.71
	C ₈ ⁼	2.68	1.768	1.03	1.19	1.40	1.38
	C ₉ ⁼	6.10	5.20	5.30	4.02	4.40	5.43
	C ₁₀ ⁼	0.19	0.03	0.25	0.02	0.21	0.22
	C ₁₁ ⁼	0.79	0.10	0.02	0.08	0.48	0.17
	C ₁₂ ⁼	0.27	1.26	0.05	0.02	0.21	0.22
	C ₁₃ ⁼	0.41	1.51	1.03	1.21	1.75	1.94

The temperatures were performed at 230, 250, 270, 290, 310 and 330 °C, with the other conditions keeping constant. The operating pressure was controlled at 6.89 MPa while the gas hourly space velocity was maintained at 4000 h⁻¹. Five (5) g of catalyst was used. The feed gas was biosyngas from gasifier (about 47 % N₂, 21 % CO, 18 % H₂, 12 % CO₂, and 2 % CH₄).

Table 2 Effect of pressure on CO conversion, hydrocarbon selectivity, hydrocarbon distribution, and liquid hydrocarbon distribution.

Pressure (MPa)		3.45	5.17	6.89	8.62
CO conversion (%)		83.7	88.3	89.8	92.3
CO ₂ selectivity (%)		11.2	11.1	9.9	8.8
Hydrocarbon selectivity (%)		88.8	88.9	90.1	91.2
CH ₄ sel. (%)		15.7	13.5	12.5	11.2
C ₂ -C ₄ sel. (%)		28.4	28	29.2	27.1
C ₅ + sel. (%)		55.9	58.5	58.3	61.7
Liquid fuel distribution (%)	Paraffins	3.7	4.8	5.15	4.5
	I-Paraffins	11.5	12.34	11.84	12.1
	Olefins	48.1	48.1	48.91	48.9
	Napthenes	9.87	7.38	5.37	4.98
	Aromatics	8.0	7.8	6.82	6.6
	Oxygenates	2.9	3.9	6.44	6.5
	C ₄ ⁼	7.90	8.15	6.91	6.36
Liquid olefin distribution (%)	C ₅ ⁼	21.64	21.81	20.02	18.14
	C ₆ ⁼	30.40	30.80	30.73	30.50
	C ₇ ⁼	34.80	34.72	35.82	37.08
	C ₈ ⁼	1.20	1.19	1.186	2.11
	C ₉ ⁼	3.62	3.06	4.01	4.18
	C ₁₀ ⁼	0.17	0.04	0.02	0.20
	C ₁₁ ⁼	0.08	0.06	0.082	0.08
	C ₁₂ ⁼	0.17	0.02	0.02	0.04
	C ₁₃ ⁼	0.02	0.17	1.21	1.33

Experiments under pressures of 3.45-8.62 MPa, were conducted. Temperature was held constant at 270 °C. The space velocity was maintained at 4000 h⁻¹. Five (5) g of catalyst was used. The feed gas was biosyngas from a gasifier (about 47 % N₂, 21 % CO, 18 % H₂, 12 % CO₂, and 2 % CH₄).

Table 3 Effect of gas hourly space velocity (GHSV) on CO conversion, hydrocarbon selectivity, hydrocarbon distribution, and liquid hydrocarbon distribution.

GHSV (h ⁻¹)		2000	4000	8000
CO conversion (%)		89.20	83.61	72.93
CO ₂ selectivity (%)		10.40	8.80	8.50
Hydrocarbon selectivity (%)		89.60	91.20	91.50
CH ₄ sel. (%)		11.00	11.20	13.90
C ₂ -C ₄ sel. (%)		25.50	27.10	26.30
C ₅ + sel. (%)		67.60	61.70	59.80
Liquid fuel distribution (%)	Paraffins	3.56	5.15	9.90
	I-Paraffins	12.50	11.84	12.20
	Olefins	49.0	48.89	38.51
	Napthenes	8.50	5.37	6.50
	Aromatics	8.20	6.82	7.0
	Oxygenates	2.80	6.44	6.60
Liquid olefin distribution (%)	C ₄ ⁼	5.03	6.91	7.17
	C ₅ ⁼	17.49	20.02	20.33
	C ₆ ⁼	32.01	30.73	34.41
	C ₇ ⁼	36.64	35.82	32.46
	C ₈ ⁼	1.85	1.19	0.91
	C ₉ ⁼	5.21	4.01	4.02
	C ₁₀ ⁼	0.57	0.02	0.08
	C ₁₁ ⁼	0.18	0.08	0.05
	C ₁₂ ⁼	0.41	0.02	0.03
	C ₁₃ ⁼	0.62	1.21	0.54

Experiments were completed with different GHSV, 2000, 4000, and 8000 h⁻¹ and the other operating conditions held constant at 270 °C, 6.89 MPa. Five (5) g of catalyst was used. The feed gas was biosyngas from a gasifier (about 47 % N₂, 21 % CO, 18 % H₂, 12 % CO₂, and 2 % CH₄).

Table 4 Typical product distribution of the C₅⁺ liquid fraction for the carbon-encapsulated iron nanoparticles nanoparticle catalyst by group type and carbon number (in mol percent).

	Paraffins	Iso-Paraffins	Olefins	Naphthenes	Aromatics	Unknowns	Total
C5	3.63	0.7	11.79	0.12	0	0	16.24
C6	0.67	0.12	16.51	0	0	1.63	18.93
C7	0.56	1.3	17.62	0.55	0	1.19	21.22
C8	0.05	1.42	0.58	1.96	0.4	6.68	11.04
C9	0.06	4.62	1.97	1.81	0.41	1.98	10.79
C10	0.22	2.4	0	0.73	4.62	1.22	9.19
C11	0.016	1.15	0.043	0.2	1.55	1.78	4.74
C12	0.0022	0.11	0	0.013	0.85	1.39	2.37
C13	0.001	0.0013	0.6	0	0	1.87	2.47
Total	5.10	11.82	49.11	5.38	7.83	17.74	96.99

Caption of the figures

Figure 1 XRD patterns of samples. a: the fresh carbon-encapsulated iron nanoparticles; b: the carbon-encapsulated iron nanoparticles calcined under a nitrogen flow at 700 °C; c: the carbon-encapsulated iron nanoparticles after catalytic reaction.

Figure 2 SEM images of samples. a: the fresh carbon-encapsulated iron nanoparticles; b: the carbon-encapsulated iron nanoparticles calcined under a nitrogen flow at 700 °C; c: the carbon-encapsulated iron nanoparticles after catalytic reaction.

Figure 3 TEM images of samples. a: the fresh carbon-encapsulated iron nanoparticles core-shell catalyst; b: the carbon-encapsulated iron nanoparticles calcined under a nitrogen flow at 700 °C; c: the carbon-encapsulated iron nanoparticles after catalytic reaction. d and e: HRTEM images of the calcined carbon-encapsulated iron nanoparticles core-shell catalyst.

Figure 4 Raman and FTIR spectra of the carbon-encapsulated iron nanoparticles. a: the fresh carbon-encapsulated iron nanoparticles; b: the carbon-encapsulated iron nanoparticles calcined under a nitrogen flow at 700 °C.

Figure 5 TG and DTG curves of the carbon-encapsulated iron nanoparticles from pine wood derived sugars heated at a rate of 10 °C/min in N₂ atmosphere (a), and TPD curves for the temperature-programmed calcination of the carbon-encapsulated iron nanoparticles from pine wood derived sugars, 5 °C/min to 700 °C purging gas: 20 ml/min nitrogen (b).

Figure 6 TEM image of the one-hour HTC sample.

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23 Figure 1 XRD patterns of samples. a: the fresh carbon-encapsulated iron nanoparticles; b: the
 24 carbon-encapsulated iron nanoparticles calcined under a nitrogen flow at 700 °C; c: the carbon-
 25 encapsulated iron nanoparticles after catalytic reaction.

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Figure 2 SEM images of samples. a : the fresh carbon-encapsulated iron nanoparticles; b : the carbon-encapsulated iron nanoparticles calcined under a nitrogen flow at 700 °C; c : the carbon-encapsulated iron nanoparticles after catalytic reaction.

Figure 3 TEM images of samples. a: the fresh carbon-encapsulated iron nanoparticles; b: the carbon-encapsulated iron nanoparticles calcined under a nitrogen flow at 700 °C; c: the carbon-encapsulated iron nanoparticles after catalytic reaction; d and e: HRTEM images of the calcined carbon-encapsulated iron nanoparticles core-shell catalyst.

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44 Figure 4 Raman and FTIR spectra of the carbon-encapsulated iron nanoparticles. a: the fresh
 45 carbon-encapsulated iron nanoparticles; b: the carbon-encapsulated iron nanoparticles calcined
 46 under a nitrogen flow at 700 °C.

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Figure 6 TEM image of the one-hour HTC sample.