

A Pilot Study of Syngas Production from Bio-oil Thermal Cracking in a Bubbling Fluidized Bed Reactor

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ABSTRACT

A fluidized bed reactor that is operating in the bubbling regime has been developed for the conversion of bio-oils to syngas.

The reactor consists of a 7.6 cm I.D. (or internal diameter) bed, with an expanded freeboard. The volume of the reactor can be adjusted to vary the gas residence time. This reactor has been used to carry out either thermal or catalytic cracking for reforming bio-oils.

A gas-atomized injector has been specially developed to feed a bio-oil, which may be viscous and contaminated with small ash and char particles. Besides, the gas-atomized nozzle allows it to remain cool until coming in contact with the fluidized particles inside the bed.

This article presents the product yields and compositions obtained by thermally cracking the bio-oil at various temperatures and gas residence times. The bed temperature was varied from 500 to 700 °C. Moreover, the vapor residence time ranged from 7.8 to 27.6 seconds.

Also, the effect of particle size and mass of bed was investigated. Finally, based on this study, the conversion of bio-oil to gas increased with an increase in temperature and residence time.

Keywords: Bio-Oil, Syngas, Hydrogen, Fluidized Bed Reactor, Thermal Cracking.

INTRODUCTION

Syngas can be produced from different resources such as natural gas, naphtha, residual oil, petroleum coke, coal, and biomass [1]. Syngas is an important chemical building block from which valuable products can be produced such as methanol, ethanol, olefins, and paraffin. While biomass contains less hydrogen than resources

such as natural gas, it is a renewable resource that releases net zero greenhouse gases into the atmosphere [2]. In fact, it can be carbon negative: Biomass converted to bio-oils produces carbon-rich biochar as a co-product; moreover, if bio-char was dispersed into the ground, it would represent a stable form of carbon sequestration. In the case of an increase in the price of fossil fuels or depletion

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of their resources, biomass can be counted as a safe and reliable resource of energy.

In addition, biomass may be converted to syngas either directly, through a gasification process, or indirectly in two steps: biomass is first pyrolyzed to produce primarily liquid bio-oil, which is then gasified to syngas. The indirect route has several advantages. The bio-oil may be generated in decentralized production facilities or mobile plants near the biomass sources, and then shipped to a central facility for conversion to syngas, avoiding the expensive transportation of bulky and perishable biomass. Also, the syngas produced from bio-oil is cleaner because fewer tar compounds are produced in comparison with direct biomass gasification [37]. In addition, tar has detrimental effects on the downstream processes. Finally, valuable green chemicals may be extracted from the bio-oil before it is converted to syngas. For example, the lignin fraction of the bio-oil could be used in producing phenol-formaldehyde adhesives or high-octane gasoline-blending components [3].

A typical biomass consists of water, cellulose, hemicellulose, and lignin. Composition of bio-oil depends on the biomass from which it was pyrolyzed, the pyrolysis conditions and whether the catalyst was used in the process. However, all bio-oils have usually similar constituents as they are generally oxygenated compounds like acids, aldehydes, alcohols, and ketones [5-8]. Bio-oil is reasonably stable at room temperature, but polymerizes even at moderate temperatures (around 80 °C), and, at higher temperatures, it decomposes. Some of the molecules of bio-oil may not even be stable at ambient temperatures [5,7,9].

The gasification of model compounds representing the major constituents of bio-oil has been studied

to identify reaction mechanisms and the impact of reaction conditions and of the presence of various catalysts. Since a bio-oil is composed of much complex molecules, e.g. lignin that does not easily crack by thermal energy, such investigations provide only useful information to screen off candidate catalysts and operating conditions for gasification of whole of a bio-oil. [4-7,10-29].

Publications on the gasification or steam reforming of actual bio-oils are less numerous than for model compounds. Because of physical properties of bio-oil such as its quick solidification inside the hot injection nozzles, there had been challenges to gasify whole bio-oils. Therefore, aqueous fraction of bio-oil, which was separated from the lignin fraction by adding excess water, was tested for syngas production taking advantage of high water content in the solution [3,30-32].

During the recent years, utilization of the whole bio-oil has been considered to produce syngas [33-42]. Most of the published literature so far have dealt with catalytic steam reforming of the bio-oils. Thermal cracking of bio-oil was considered as a route to produce product gases with high heat values [33,34], but the limited publications about bio-oil thermal gasification reported low bio-oil conversion and syngas yield in the absence of catalyst [36,37,40].

As the first step of the experimental work of this research, thermal cracking of the whole bio-oil was investigated. The objective of this work was to investigate a practical process for the conversion of the whole bio-oil into syngas, using a fluidized bed of inexpensive, attrition-resistant silica sand, and operating at low pressure, and temperatures (500 to 700 °C) with varied vapor residence time (8 to 28 seconds). It was to understand whether

it was possible to increase bio-oil conversion through a thermal cracking process. There was not any literature report of gasifying the whole bio-oil at the time. This investigation included designing an efficient bio-oil feeder for long run continuous experiments. Furthermore a downstream separation system was designed to maximize separation of the condensable products in a condenser, and separate the fine oil droplets from the stream of the permanent product gases, which did not stay in the condenser. Finally, the obtained results of this research would enable us to identify strategies to improve the gasification process in terms of operating conditions, catalysis, and reactor configurations.

Pilot Plant Setup

The Institute for Chemicals and Fuels from Alternative Resources (ICFAR) has designed and set up a fluidized bed reactor, operating in the bubbling regime, for the conversion of bio-oil to syngas. The reactor consists of a 0.076 m I.D. bed column made of stainless steel, with an expanded freeboard, whose volume may be adjusted to vary the gas residence time. This reactor can be used to carry out either thermal cracking or catalytic cracking/reforming bio-oil. Figure 1 shows a schematic diagram of the gasification pilot plant. In order to feed bio-oil at a continuous and fixed flow rate into the reactor, a special hydraulic pumping system is employed in which there is a reciprocating piston inside a cylinder. In addition, hydraulic oil is pumped by a fixed flow rate to push the bottom of the piston upward so that bio-oil that is stored on the top of the cylinder is fed into the reactor. During normal operation of the pilot plant, the pressure supplied by the pump is about

60 psig. This hydraulic system is shown in Figure 2. A spray nozzle was designed to address two conflicting concerns: thermal degradation of the bio-oil and excessive cooling of the fluidized bed near the injection zone. An initial design of a water-cooled nozzle resulted in cooling not only of the nozzle but also of the fluidized bed, whose local bed temperature dropped by 20 to 30 °C. Moreover, experiments without cooling water showed that the bio-oil temperature raise never passes 200 °C in the nozzle. On the other hand, thermal stability experiments showed that, in the presence of oxygen, bio-oil quickly degraded at temperatures as low as 100 °C. However, there was no degradation of the bio-oil at 200 °C under a nitrogen blanket. The spray nozzle was, therefore, used without water cooling and with nitrogen as atomization gas.

Either nitrogen or steam can be preheated by furnaces and then used as atomization and fluidization medium. In case of steam reforming, still water passes through the furnace, and then is superheated up to 300 °C. In this work, nitrogen was only used as fluidization and atomization gas. Atomization nitrogen was not preheated and was mixed with bio-oil at the nozzle tip. Sugar solution with physical characteristics of density and viscosity similar to bio-oil was used to test flow rate of nitrogen versus quality of spray. The appropriate flow rate of nitrogen which is required to efficiently spray the sugar solution was about 5 standard liters per minute. Figure 2 shows how the nozzle was designed. The central tube of the nozzle through which bio-oil was pumped to reactor had an I.D. of 0.015 m. Fluidizing nitrogen was heated up to reactor temperature inside reactor windbox, and then passed through a grid to fluidize the bed

material. Feed injection point, where the nozzle tip is located, was 0.18 m above the grid.

If bio-oil stays stagnant inside the nozzle, it can plug the nozzle easily because of two reasons: it either sticks to solid particles or it burns with air and then coke is formed along the tube of the feeding nozzle. In order to avoid having these problems, after each run the nozzle was flushed with an ethanol flow to wash the remaining bio-oil into reactor, followed by a flow of nitrogen. In addition, before starting to pump bio-oil towards the nozzle, a continuous flow of nitrogen inside the central tube of the nozzle prevented solids from entering and plugging the nozzle.

The reactor consisted of a cylindrical section with an I.D. of 0.078 m and a height of 0.52 m, topped by an expanded section whose diameter and height was varied to obtain different residence times of gases inside the reactor. Band heaters were used to heat up and keep the reactor at the desired reaction temperature and thermocouples were used to measure the reactor temperature at different levels. The reactor was surrounded by two 0.05 m thick layers of insulation: an inner layer of Fiber Frax and an external layer of covered glass wool.

Product gas entered a cyclonic condenser, immersed in an iced water tank, where water and bio-oil liquids including tars were condensed. The condenser was made of aluminum with I.D. of 0.076 m and height of 0.91 m. Since the condenser was immersed completely inside a cold-water tank, its wall temperature was as cold as the equilibrium temperature of the tank. Outlet vapors from reactor entered condenser from the top through a short tube (0.01 m I.D. and 0.05 m downward from the top bent with a 45° angle); therefore, gases hit the

internal wall of the condenser at the top and started a spiral flow until they arrived at the bottom of the condenser. Non-condensable gases would leave the condenser through another 0.01 m I.D. tube which was hanged from the top, and its bottom had 0.013 m distance from the bottom of the condenser. This design helped fast condensation of gases and easy separation of liquid products from non-condensable gases (Figure 1). There was also one by-pass condenser which was used before running an experiment. After non-condensable gases exited the condenser, fine liquid droplets were recovered with an electrostatic precipitator (ESP). More details of the design of the ESP can be found elsewhere [43]. Gases exiting the ESP were further filtered, and then either vented or collected in Tedlar gas sampling bags for subsequent analysis. An HP 5890 gas chromatograph with a thermal conductivity detector was used to analyze the product gas (H_2 , CO, CO_2 , CH_4 , and N_2). Nitrogen was used as an internal standard gas to determine the flowrate of product gases. During the experiments designed to investigate the effects of residence time on gasification yield, a 2-m long RESTEK Shin Carbon ST (micro packed) column with 0.001 m ID (internal diameter) and 0.0016 cm OD was used, with argon as the carrier gas, in the gas chromatograph. When studying the effect of temperature on thermal cracking of bio-oil, a molecular sieve column followed by a silica gel column in series was used, with helium as the carrier gas, and an automatic Valco valve changed the direction of the gas flow through the columns to detect all gas components. The molecular sieve column was used for detecting H_2 , N_2 , CH_4 , and CO while the silica gel column was used to detect CO_2 . The Valco valve was programmed to switch the

carrier gas flow from the silica gel-molecular sieve direction to the molecular sieve-silica gel direction after the CO was completely eluted.

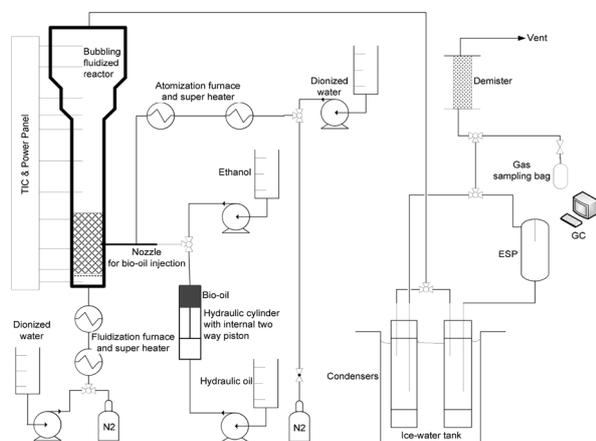


Figure 1: Schematic diagram of the bubbling fluidized bed setup.

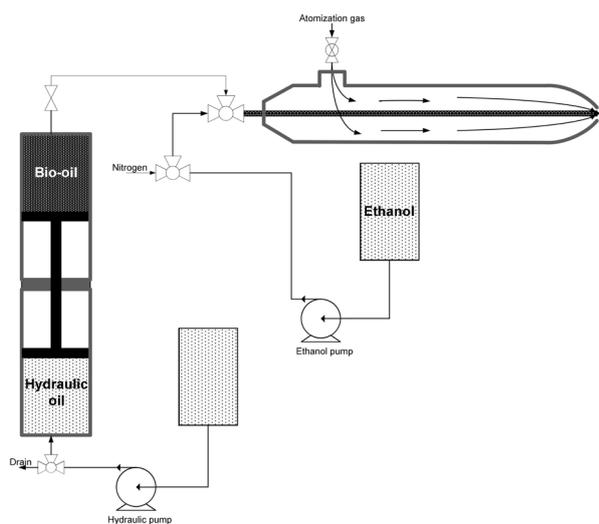


Figure 2: Hydraulic pumping system and nozzle assembly to feed bio-oil into reactor.

EXPERIMENTAL PROCEDURE

Nitrogen was used to fluidize reactor particles and to spray-atomize bio-oil into the reactor bed. The nitrogen flowrate could be adjusted by mass flow meters. The fluidized bed provided very good contact for bio-oil droplets to the hot solid particles to achieve high rates of heat and mass transfer; also, solids back mixing within the bed ensured a uniform bed temperature. After each

run, coke deposits on the bed particles could be easily burned off with air.

Silica sand ($\rho_p=2650 \text{ kg/m}^3$) was used as the bed material. As per Geldart's solid particles classification, bubble properties within the fluidized bed, and, hence, heat and mass transfer are greatly different for Geldart's groups A and B. Two different silica sands were, therefore, used to determine that there were no significant mass or heat transfer limitations: sand with a Sauter mean diameter of $80 \mu\text{m}$ representing Geldart's group A particles and sand with a Sauter mean diameter of $200 \mu\text{m}$ representing Geldart's group B particles. In addition, a bed mass of 1.5 kg of silica sand was used for most experiments. Silica sand is not a porous solid and it is mainly used as inert bed material for good mixing and heat transfer purposes. To check for possible catalytic activity of the sand, some selected experiments were repeated with 3.0 kg of silica sand.

The thermal cracking experiments were conducted over the temperature range between $500 \text{ }^\circ\text{C}$ and $700 \text{ }^\circ\text{C}$. The lowest temperature, $500 \text{ }^\circ\text{C}$, was the temperature that was used to produce the bio-oil from hardwood pyrolysis. The highest temperature, $700 \text{ }^\circ\text{C}$, corresponds to the maximum temperature that could be achieved with a reactor build of the inexpensive steel. The reactor pressure was just above atmospheric pressure.

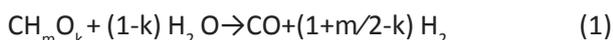
While the reactor was being heated up to the set-point temperature, an airflow was used to keep the bed at the minimum fluidizing condition. Furthermore, to prevent plugging of the spray nozzle with solids, another air flow was maintained through atomization and internal feeding tube of the nozzle. At the start of a run, all air streams were switched to nitrogen. While the by-pass condenser

was in operation, injection of bio-oil started to avoid collecting liquids in the main condenser in case of likely malfunction of the bio-oil nozzle. After the proper bio-oil injection was ensured, the product gas stream was switched from the by-pass condenser to the main condenser. After each experiment, the product stream was switched back to the by-pass condenser and bio-oil was replaced by ethanol to clean the feeding system.

Gasification Reactions

Bio-oil is a complex mixture of oxygenated compounds, such as acids, alcohols, aldehydes, esters and ketones. Its water content varies between 20 and 30 wt%. Including its water content, bio-oil can be represented by a general formula such as CH_mO_k . Syngas production processes are also called steam reforming processes, because steam is added to the reactor to react with the feed at sufficiently high temperatures to produce hydrogen and carbon monoxide. To increase the steam concentration in the reacting gases, additional steam can be added as fluidization medium, beyond the water naturally contained in the bio-oil. In the current study, however, no additional steam flow was used, and the only steam present in the reactor came from the water contained in the injected bio-oil.

In the presence of steam, bio-oil with the general formula of CH_mO_k (neglecting the nitrogen content) can be converted to syngas (H_2+CO) according to Reaction 1 which is an endothermic reaction:

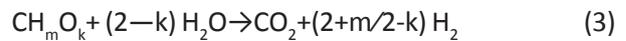


If there was enough steam in the reactor, the produced CO would react with steam through the water-gas shift reaction to produce more hydrogen:

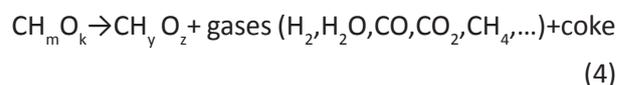


Therefore, summing up Reactions 1 and 2, the

overall steam reforming of bio-oil can be expressed by Reaction 3:



There are several other reactions which take place after bio-oil is injected into the reactor. For example, as soon as bio-oil is entered into the reactor, it decomposes thermally to other forms of the oxygenated molecules (CH_yO_z) as well as some permanent gases (hydrogen, steam, CO, CO_2 , and light hydrocarbons) and coke (Reaction 4). It is claimed by Czernik et al. in 2002 that the carbon-oxygen bonds of bio-oil make it more reactive when it is compared with hydrocarbons. Thus, some components, like furans, phenols, and carbohydrates, which are unstable at high temperatures, react with carbon deposition [3]. Moreover, the Boudouard reaction (Reaction 5) is another important reaction which can affect the CO/ CO_2 ratio in the final product gases because CO, CO_2 , and coke are available inside the reactor.



In addition, in the presence of steam, the produced hydrocarbons might undergo steam reforming reactions towards the production of hydrogen and carbon monoxide. For example, Reactions 6 and 7 illustrate how methane can be converted to syngas:



At higher temperatures, methane production is decreased. Also, the partial pressure of steam affects the conversion of methane to syngas.

RESULTS AND DISCUSSIONS

Results presented here were obtained by thermal gasification of a bio-oil that was produced by

pyrolysis of hardwood at moderate temperatures, in the absence of oxygen, at the Dynamotive Energy Systems Corporation in Canada. Table 1 lists elemental analysis, general formula and high heat value of this bio-oil.

Table 1: Elemental analysis and HHV of Dynamotive bio-oil.

C, wt.%	H, wt%	O, wt.%	CH _m O _k	HHV, kJ/kg
41.67	7.20	51.13	CH _{2.07} O _{0.92}	15,696

The nitrogen flowrates were the same for atomization and fluidization, at 4.5 standard liters per minute at reactor conditions. To keep the same residence time for all experiments, the flowrate of nitrogen was adjusted according to the temperature of each run. The voltage applied to the ESP was 1.8 kV to collect all mists from the product gas.

Also, initial experiments were carried out to investigate the effect of vapors residence time on the yield of bio-oil gasification products. Then, once the most appropriate vapors residence time was identified, the effect of temperature on product yields was investigated.

The yield of each individual gas has been reported as the number of moles of the produced gas per gram of the total bio-oil injected during the reaction. The yield of total gas products (H₂, CO, CO₂, and CH₄) as well as the yield of liquid products, were calculated as total mass the collected product per total mass of the total bio-oil injected during the reaction.

Effect of Residence Time

It was assumed that the vapor residence time was equal to the total time that the gas should have traveled through the fluidized bed and the

freeboard. The gas should follow a pattern close to the mixed flow characteristics inside the bubbling fluidized bed and a pattern similar to plug flow along the freeboard; however, a plug flow was assumed for both the fluidized bed and the freeboard as the objective of this research was to investigate the relative impact of the free-board volume on bio-oil conversion. In other words, the effect of residence time was studied by changing the freeboard volume for a given flowrate of bio-oil and nitrogen.

Three residence times were investigated: 7.8, 11.4, and 27.6 seconds. The flow rate of bio-oil was 2 mL/min. Experiments were conducted at 600 °C and 700 °C for 10 minutes, and the product gas was sampled at the end of each test. The preliminary tests had shown that the composition of the product gases did not change within the initial 10 minutes.

Yield data in Figure 3 showed that residence time plays an important role in syngas production. Total gas production increases with longer residence times. The yield of (H₂+CO) at the longest residence time is almost doubled when compared to that achieved at the shortest residence time. A longer residence time has also a very beneficial effect on the molar H₂/CO ratio. The effect of longer residence times at higher temperatures is even more significant. This means that there are more thermally unstable compounds at elevated temperatures, and when they are staying longer inside the reactor, the rate of thermal cracking increases in favor of hydrogen production.

As a result, the next series of experiments designed to investigate the effect of temperature on bio-oil gasification were conducted at the residence time of 27.6 seconds.

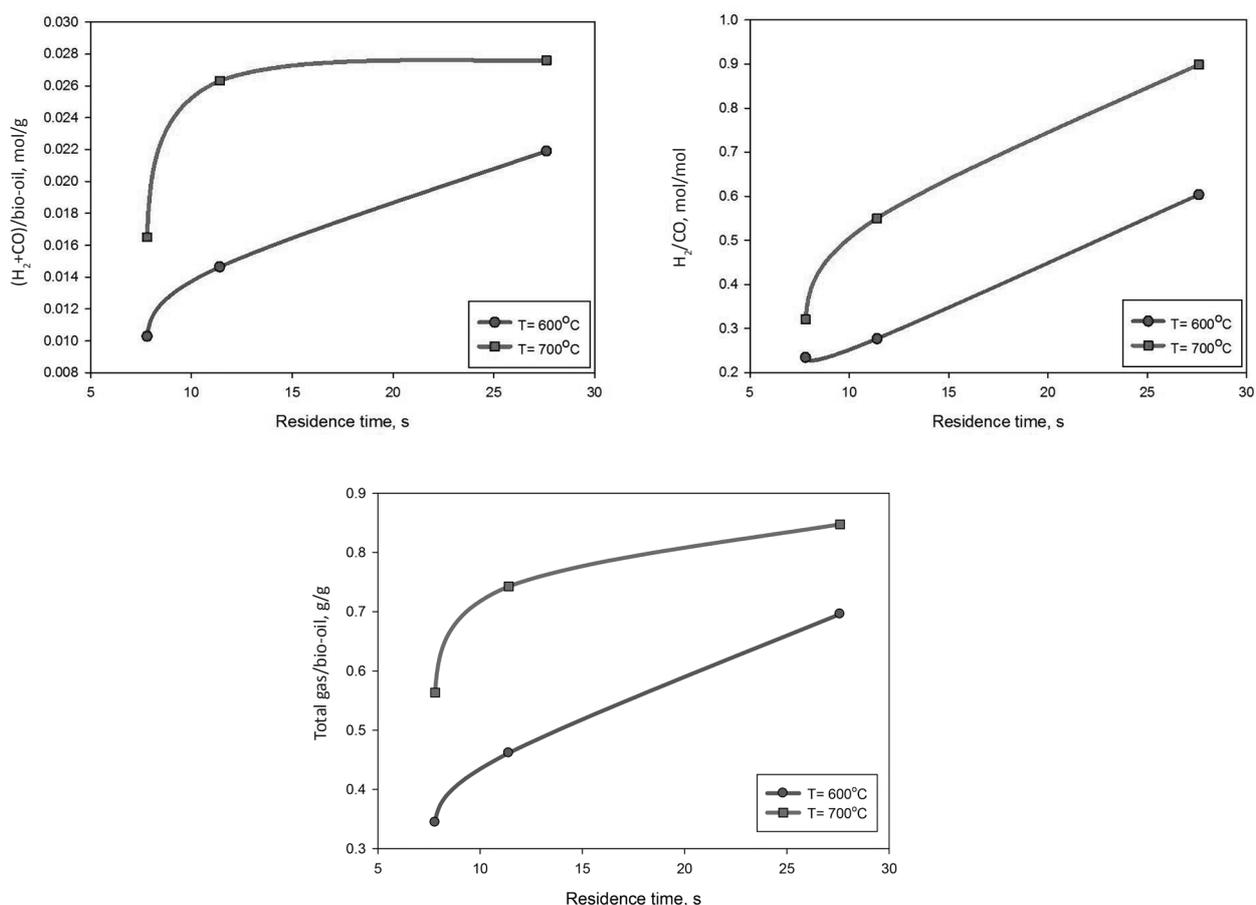


Figure 3: The yield of gases and molar H_2/CO ratio versus residence time; the mass of the sand bed: 1.5 kg, Sauter mean diameter of the sand: 200 μm .

Effect of Temperature

Preliminary experiments have shown that the composition of product gas evolves with time during long runs. There are two possible reasons: the sand may have catalytic activity and becomes deactivated by coke deposits, or the coke deposits themselves may have a catalytic activity. It was, therefore, decided to run each test for one hour to clearly characterize the evolution in gas production and gas composition: bio-oil flow rate was 4 mL/min for these experiments. The product gas was sampled after 5, 30, and 60 minutes. Also, bed samples showed negligible coke deposits after 5 minutes

while, after 60 minutes, the bed particles were completely covered with coke.

In Figure 4, experimental data presents the yield of permanent gases over the temperature range of 500 °C to 700 °C during one hour of operation for group B and group A solids. The hydrogen yield is similar for group B and group A sands, confirming that there are no significant heat or mass transfer limitations. It is suggested by Reaction 1 that higher temperatures increase hydrogen production. At all temperatures, there is a dramatic drop in hydrogen production with time.

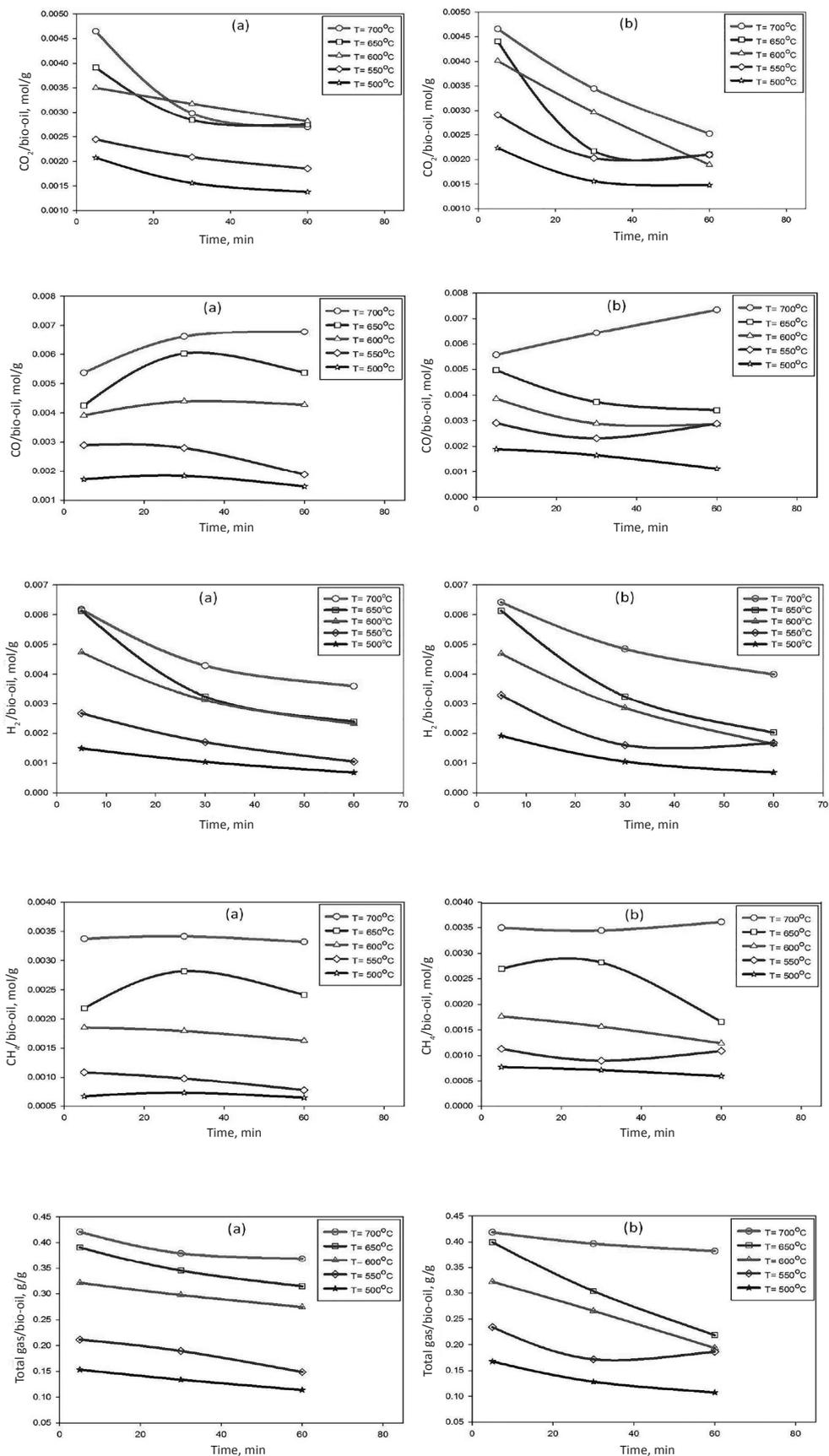


Figure 4: The yield of product gases versus time on stream; the mass of the sand bed 1.5kg, Sauter mean diameter of the sand: (a) 200µm, (b) 80 µm.

The yield of carbon monoxide also increases with temperatures. It seems difficult to determine how CO production evolves with time.

Finally, the results showed that at higher temperatures CO production increases with time while at lower temperatures, this trend is reversed. There is also a difference between group A and B solids at intermediate temperatures.

In addition, carbon dioxide follows the same trends as hydrogen production. More carbon dioxide is produced at higher temperatures. Also, carbon dioxide production also drops dramatically with time.

Methane production increases with increasing temperature. There is no definitive evolution of methane production with time.

The positive effect of temperature on the production yield of all gases indicated that kinetics rather than thermodynamics controls the reaction. For example, the water gas-shift reaction is exothermic, and, if there was thermodynamic control, increasing the

temperature should reduce the production of CO and increase the production of H₂ and CO₂. The reverse results were observed. Results indicated the complexity of kinetics of the chemical reaction requiring further investigation in the future.

The total gas production decreased with time, and increases with increasing temperature. The maximum yield was about 42 % for both solid sands at 700 °C, the highest temperature, and it dropped to 37-38 % after one hour.

After each experiment, condenser and ESP were weighed to measure the mass of liquid collected in one hour. More liquid was collected in the condenser than in the ESP, as shown in Figure 5. The condenser liquid is mainly aqueous and has a dark brownish color at lower temperatures and becomes lighter at higher temperatures, indicating the concentration of very heavy compounds decreases at higher temperatures. On the other hand, the ESP liquid is an oil phase.

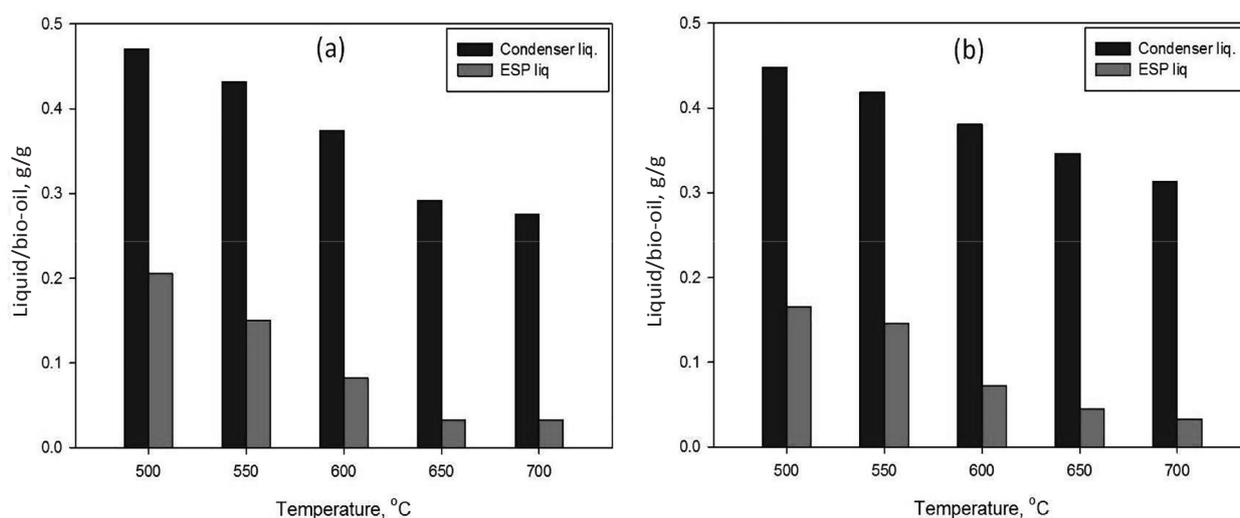


Figure 5: The yield of liquid production; Mass of the sand bed 1.5kg, Sauter mean diameter of the sand: (a) 200μm, (b) 80 μm.

Figure 5 shows that similar results were obtained for group A and B beds, suggesting that liquid conversion was not significantly affected by any heat or mass transfer limitation.

Moreover, it has been estimated that between 20 wt.% and 30 wt.% of bio-oil injected is converted into coke. It can be concluded that coke formation is a main cause of the reduction with time of the yield of total gases.

Effect of Bed Mass

Because the freeboard temperature was similar to the bed temperature, thermal cracking occurred equally in the bed or the freeboard. Therefore, doubling the bed mass should only affect catalytic cracking. In Figure 6, experimental data shows the results of gasification experiments performed at 600 °C, 650 °C, and 700 °C with a sand mass of 3.0 kg. The trends were the same as with the lower bed mass, i.e. 1.5 kg.

Doubling the bed mass did not greatly increase the total yield of dry gases. At 700 °C, for example, this total gas yield was only increased by around 3%, which could be due to the longer residence which was provided in the bubbling bed by doubling the bed mass. This confirms the results obtained with the two particle sizes, since increasing the specific surface of the sand particles by a factor of 2.5 did not greatly affect gas production. Therefore, the sand particles did not have a significant catalytic effect.

One possible source of the yield decrease upon the reaction duration might be the drop of the bed temperature due to the endothermic reactions even though the thermocouples along the reactor recorded very moderate temperature fluctuations around the set-point, i.e. +/- 20 °C. This can be

more pronounced in the freeboard where the gas has a plug flow.

Since fine coke particles were distributed through the freeboard, it is also likely that the dramatic drop in reactor performance with time was caused by a detrimental catalytic effect of the coke particles. The experiments were carried out for a duration of 1 hour. So, some tests for a much longer duration, e.g. 24 hours, would reveal whether the bed would reach a stable performance, or it would keep the declining performance.

Effect of Particle Size

As discussed, two different solid sand sizes were used to determine whether there were significant heat or mass transfer limitations, since heat and mass transfer rates are much higher with the smaller particles [44]. For instance, smaller bubbles were formed in a bubbling with Geldart's group A particles than with group B particles, the associated mass transfer rate should be higher due to the provision of the larger surface area.

The total initial gasification yield for each experiment was compared with the two types of sand, as shown in Figure 7. Although there are minor differences, results obtained with group B and group A solids are very similar. Therefore, it can be concluded that there were no significant heat or mass transfer limitations.

In addition, Figure 7 illustrates that, at the best condition, total conversion of bio-oil to gaseous products was less than 45%. Therefore, in order to increase conversion of bio-oil to gaseous products, the effect of additional steam, of elevated temperatures and of appropriate catalysts must be investigated.

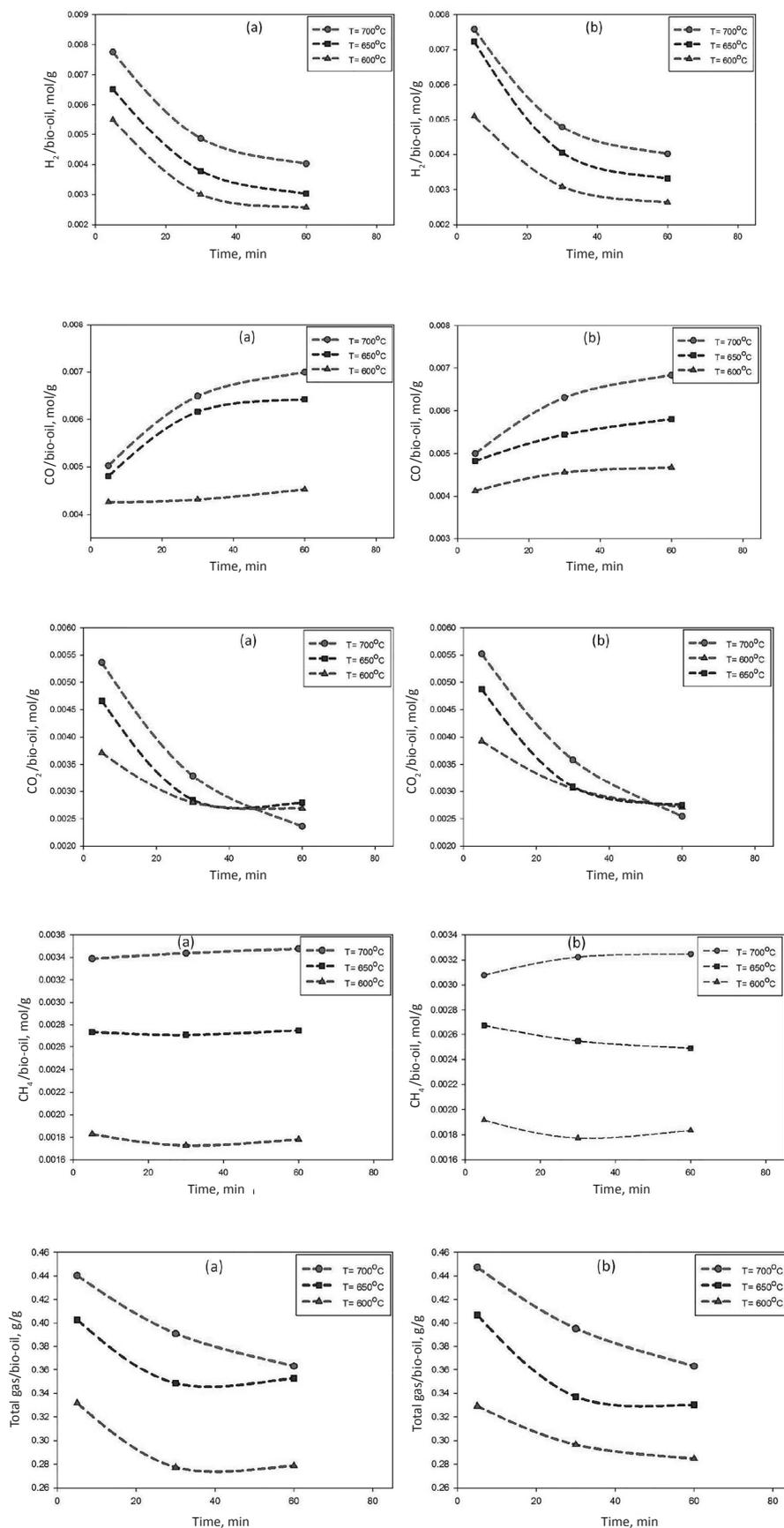


Figure 6: The yield of product gases versus time on stream; the mass of the sand bed 3.0kg, Sauter mean diameter of the sand: (a) 200µm, (b) 80 µm.

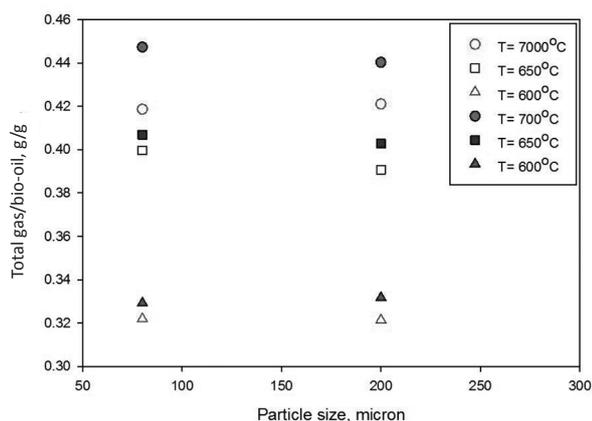


Figure 7: Effect of sauter mean diameter of the sand on total yield of gasification. Empty symbols: the mass of bed 1.5 kg, bold symbols: the mass of bed 3.0 kg.

Syngas (H₂+CO) Production

The two gases of economic interest for conversion to other products are hydrogen and carbon monoxide. Figure 8 shows that the rate of syngas production increases with an increase in temperature. Also, it decreases moderately with time.

The molar H₂/CO ratio is usually an important parameter in reforming processes, and all processes would require ratios higher than that obtained in this study. For instance, a molar H₂/CO ratio of 2 is required for methanol synthesis. This ratio dropped dramatically with time; as it was seen before, the concentration of CO tends to increase by time while the concentration of hydrogen reduces by time. Bed mass also had little effect on the molar H₂/CO ratio.

No excess steam was injected into the fluidized bed reactor in this research. A further research must be carried out to whether an excess steam would result in a high enough molar H₂/CO ratio upon thermal cracking of bio-oil.

As depicted in Figure 5, a considerable liquid is collected inside the cyclonic condenser that has a water content of above 90 wt.%. This liquid might

be recycled and fed to the reactor along with the fresh bio-oil.

In addition, another option would be an operation at temperatures above 700 °C that thermodynamically favor larger yield of syngas.

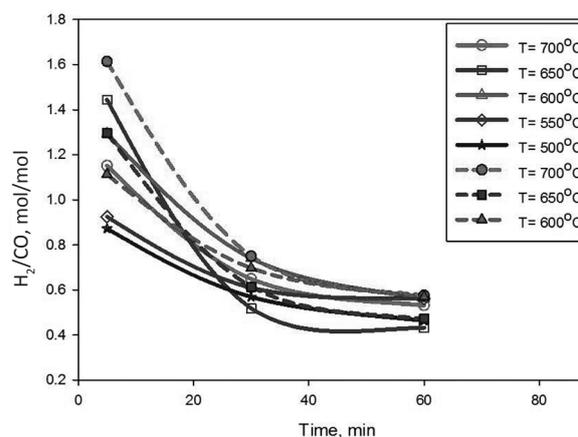
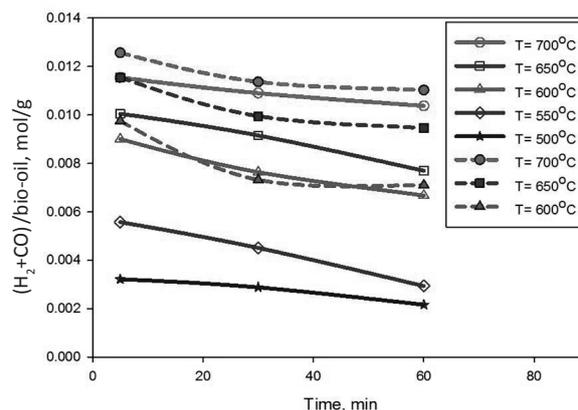


Figure 8: The yield of syngas (CO+H₂) and molar H₂/CO ratio; solid lines: the mass of bed 1.5kg, dashed lines: the mass of bed 3.0kg; Sauter mean diameter of the sand: 200 μm.

CONCLUSIONS

Thermal cracking of whole of bio-oil was investigated in a bubbling fluidized pilot plant over a temperature range of 500 to 700 °C. The effects of gas residence time, temperature, bed mass, and particle size on thermal cracking of bio-oil were studied. Longer residence times promote further cracking in the reactor, and as a result,

more syngas is produced, and the H_2/CO ratio is higher. Coke must have a detrimental effect on the kinetics of the gasification because the higher yield of gasification was obtained at the beginning of experimental runs when deposition of coke in the bed was negligible, but, with the time that coke is deposited on the surface of the sand, the yield of gasification declines. Higher temperatures always favor gasification yields, especially during the initial times of operation. In addition, liquid yields show that at low temperatures, bio-oil conversion is very poor. At the operating conditions studied, kinetics always control the thermal cracking reactions, and the system is far from thermodynamic equilibrium. The total yield of gasification was increased, not significantly though, after the bed mass was doubled which is probably due to the fact that mass ratio of deposited coke to sand became less and, as a result, the detrimental effect of coke on the gasification kinetics was reduced. Results obtained using either Geldart's group B and group A sand were very similar, indicating no heat and mass transfer limitations in the bed.

In addition, the total product gas yield was less than 45 % under applied operating conditions where the production of combustible gases such as methane and carbon monoxide was relatively significant. Whether a mixture of hydrogen and carbon monoxide or only hydrogen is of interest in the process, utilization of an appropriate catalyst and a larger steam to carbon ratio should be investigated to maximize the bio-oil conversion and yield of the product.

Such a quite low bio-oil conversion may not seem promising. However, with respect to the yield of liquid products of condenser and ESP and the yield of combustible gases, this level of conversion

might be enough in favor of a sustainable thermal process where syngas, an operation water, and an upgraded bio-oil is produced. Finally, it should be investigated whether a recycle of the operation water and its co-feeding with bio-oil into the gasifier would increase the syngas yield or not.

NOMENCLATURES

ICFAR	: Institute for Chemicals and Fuels from Alternative Resources
ESP	: Electrostatic Precipitator

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