PROCESS DESIGN AND CONTROL

Design, Construction, and Operation of a Transported Fluid Bed Process Development Unit for Biomass Fast Pyrolysis: Effect of Pyrolysis Temperature

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The objective of this paper is to investigate biomass fast pyrolysis process in a novel once-through transported fluid bed process development unit. The main emphasis was given to the design and operation of this unit, which is made of several vessel modules. The main part of the unit is a specially designed mixing zone, where the solid heat carrier mixes with the biomass feed. The unit can process up to 20 g/min biomass and can circulate up to 300 g/min solid. Experiments showed that the unit could run effectively, with satisfactory stability and mass balances (92−96 wt % on biomass), under a wide range of experimental conditions. The yield of the raw total liquid product was up to 78 wt % on biomass basis. The effect of pyrolysis temperature on product yields is also presented in this paper: the temperature of 500 °C was found to be an optimum temperature for the maximization of the liquid product yields using a wood-based biomass.

1. Introduction

Biomass has been identified as an alternative sustainable source of renewable energy. Among various technologies for the conversion of biomass to energy or to other materials (fuels, chemicals), fast pyrolysis is the most promising for industrial implementation.[1] Biomass fast pyrolysis (BFP) is the thermal decomposition of biomass in an inert atmosphere using high heating rates and short residence times, of both solids and volatiles, at temperatures between 450 and 550 °C.[2] In the BFP process, biomass is converted to vapors, gases, and char. The vapors condense to a liquid product called bio-oil. The selectivity of the process on various pyrolysis products varies, depending on the operating conditions. However, the main objective in a fast pyrolysis process is the maximization of the bio-oil yield. Bio-oil can be used either as a fuel for the production of heat or electricity,[3] or as a transportation fuel after upgrading, either through hydrogenation[4] or through gasification, followed by Fischer−Tropsch synthesis.[5] Bio-oil is also a very important source of renewable chemicals and thus, biomass fast pyrolysis is considered to be a key process in the biorefinery of the future.[6]

According to previous work, the bio-oil production and quality can be optimized by properly selecting technologies and operating variables.[7−11] It can be concluded that the main process variables that could affect the product yields, selectivities, and quality are the temperature, the heating rate (or equivalently, the biomass particle size), and the fast quenching of the vapors in order to prevent secondary cracking of the bio-oil components to lighter gaseous products.[12] Based on these principles, several reactor configurations have been proposed in the literature, aiming at the maximization of the liquid yields.[7]

The oldest reactor type for BFP is the bubbling fluidized bed, which ensures high heat transfer rates from a solid heat carrier to the biomass particles.[13] Since 1990 many large-scale pilot plants have been constructed worldwide based on fluid bed technology. An example of such a process is the Union Fenoza unit in Spain[14] with a capacity of 250 kg/h. Circulating fluid bed reactors (CFBs) or transported bed reactors have also been widely studied.[10,15] Large-scale installations of CFB technology have operated by Red Arrow Products Inc. in Wisconsin. A CFB unit was also developed at Battelle's Columbus Laboratories focusing mainly on biomass gasification.[16] The Rotating Cone Reactor (RCR) technology, developed by Biomass Technology Group (BTG) B.V.,[17] is the only European technology for biomass flash pyrolysis with effective performance in a scaling-up reactor system (250 kg/h). The principles of RCR are based on the CFB reactor. Other reactor types with a variety of applications are the vortex and ablative type reactors,[18,19] the cyclonic reactors,[20] the vacuum pyrolyzers,[21] and the entrained flow reactors. Generally, in the 1990s several fast pyrolysis technologies were studied on a pilot or demonstration scale and approached a state of commercial status. However, the majority of these plants are not currently in operation mainly due to economic reasons. Today only the Dynamotive in Canada and BTG in Europe have announced demonstration installations with high biomass capacity of 2−4 tons/day.[12]

In this work a detailed description of the construction, design, and operation of a biomass fast pyrolysis process development unit, implementing the transported fluid bed reactor technology, will be presented. This unit was originally designed as an oil-shale retort,[22,23] and it was modified to a biomass pyrolyzer under the European Energy project BIOCAT (ENK6-CT2001-00510). Previous work was conducted in CPERI on biomass pyrolysis utilizing a CFB reactor after the proper modification of an existing fluid catalytic cracking (FCC) unit.[24] The main problem with this unit was that its unstable operation under the modified operating conditions resulted in poor mass balances. Based on the experience gained from this study, a new unit has been constructed, with a flexibility to operate under a wide range of different biomass feeds and solid carriers.
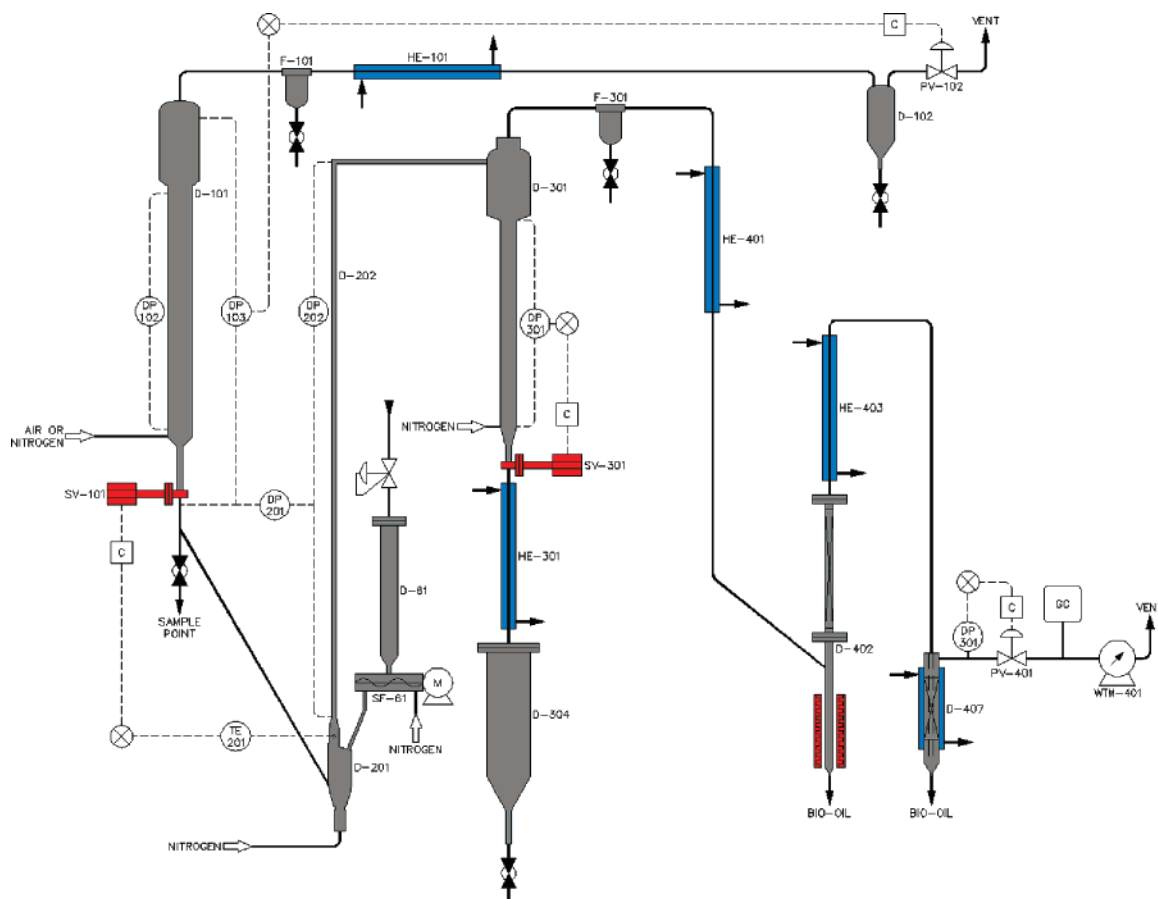
Figure 1. Schematic diagram of a process development unit for biomass pyrolysis. D201, mixing zone; D202, riser reactor; D101, regenerator; D301, stripper; D-304, solid heat carrier collection vessel; D61, biomass hopper; D-402, bio-oil first collection vessel; D-407, bio-oil second collection vessel; D-102, water collection vessel; F-101, flue gas filter; F-101, pyrolysis gas filter; HE-1, heat exchanger at regenerator exit; HE-401, heat exchanger at stripper exit; HE-403, heat exchanger at stabilizer; WTM-401, wet test meter for pyrolysis gas measurement.

Table 1. Process Development Specifications

operating variable	effective range
biomass feed rate	30−60 mL/min
biomass particle size range	50−800 μm
reactor temperature	400−600 °C
reactor pressure	1.7−3.0 atm
stripper temperature	500−600 °C
regenerator bed temperature	<680 °C
regenerator capacity	<30 L
solid circulation rate	100−300 g/min
feed hopper capacity	<3 L
vapor residence time	1 s

2. Experimental Section

2.1. Experimental Unit Description. In Figure 1 a detailed schematic view of the pyrolysis unit is presented, while in Table 1 its process specifications are listed. The entire experimental system is divided into five sections, which are discussed in the following paragraphs.

2.1.1. Biomass Feed. The biomass feed section consists of a 4 L cylindrical hopper made of PVC and glass (D-61 in Figure 1) and a variable speed screw feeder (SF-61). A pneumatic vibrator is attached on the feed hopper in order to facilitate the flow of the solids particles. The biomass feed is loaded into the feed hopper and is fed into the reactor mixing zone (injector) using the screw feeder. The feed hopper is pressurized with nitrogen, and a pressure control valve ensures that the feed hopper pressure is always higher than the injector pressure while the nitrogen fluidizes the biomass.

2.1.2. Solids Feed. The solids feed system consists mainly of a 30 L heat reactor vessel (D-101) in Figure 1 made of 316SS

material. The exit line from the heat carrier vessel includes a filter (F-101), a heat exchanger (HE-101), a slide valve (SV-101), and a pressure control valve (PV-102). The purpose of the regenerator (referred to also as the heat carrier vessel) is to regenerate the spent solids that have been used in a previous experimental run and to supply the solids with the required heat for the biomass pyrolysis reactions. The vessel is heated externally by controlled wall heaters. The gas (flue gas or nitrogen), which exits the top of the regenerator, passes first through a 5 μm hot filter (F-101) (for solids removal) and then is cooled by a heat exchanger (HE-101). Water vapors produced during the regeneration step are condensed in the heat exchanger and collected in the knockout drum (D-102). Finally, the gas is vented through a controlled valve (PV-102), which controls the pressure in this section. The regenerator is connected to the reactor through a heated transfer line, and a slide valve (SV-101) controls the solids flow to the reactor during the experiment. Samples of the regenerated solids can be withdrawn during the experiment from the bottom of the regenerator.

2.1.3. Reactor. The reactor is made of 316SS and consists of two parts: the injector (D-201) and the riser (D-202). The injector is designed to promote the direct mixing of the hot solids with the biomass particles. In addition, a stream of preheated nitrogen is introduced from the bottom of the injector to aid the transportation of the solids mixture into the riser reactor. The riser is a 5 m long vertical tube of 6.2 mm internal diameter. Pyrolysis reactions initiate in the injector and continue along the riser. Thermocouples have been installed in order to record the internal temperature of both the injector and the riser. In
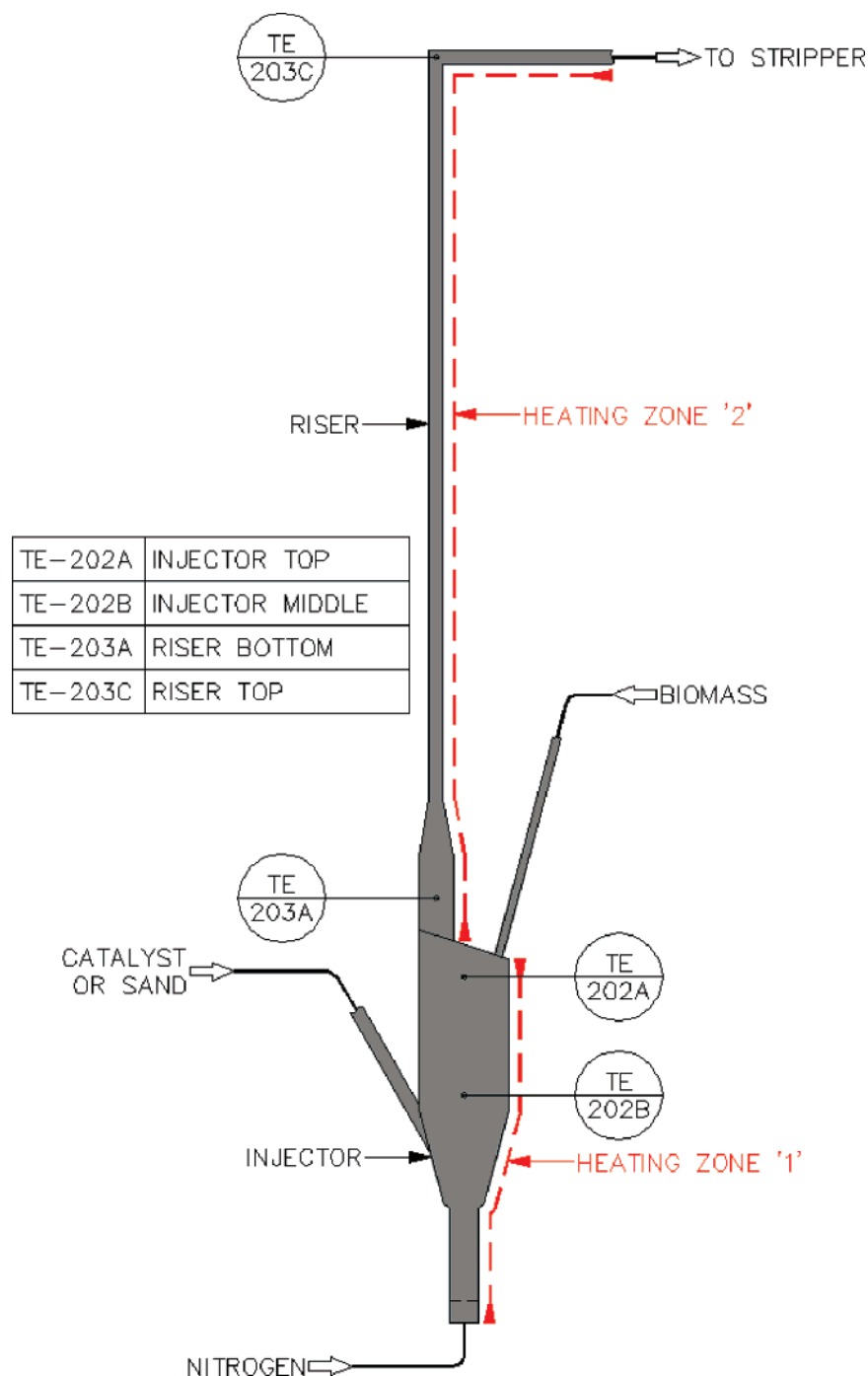
Figure 2. Reactor details: thermocouples and heating zones. Thermocouple positions are mentioned in the figure.

addition, wall heaters that supply part of the heat required for pyrolysis cover both vessels (Figure 2). The pressure drop along the injector and riser, which is indicative of the solids flow through these vessels, is recorded by differential pressure cells (DP-202). In addition, the riser bottom temperature is controlled by opening the regenerator slide valve through a temperature controller (TE-201).

2.1.4. Stripper and Solids Recovery. Gases and solids leaving the riser enter tangentially into the cyclonic head of the stripper (D-301) that performs solids removal. Nitrogen is used in the bottom of the stripper to strip off trapped vapors within the solid in the standpipe. Gases, together with entrained fine particles leaving from the top of the stripper, pass further through a hot filter (F-301) of 5 μm before moving into the liquid product recovery section. A multipoint thermocouple

inside the stripper records the temperature profile of the solids bed. In addition, the solids inventory is monitored by a differential pressure controller (DP-301). Solids removal rate is adjusted by a slide valve (SV-301) so that a constant bed height is maintained. Solids leaving from the bottom of the stripper are cooled by a heat exchanger (HE-301) and collected in a spent solids tank (D-304), where their weight is recorded by a load cell.

2.1.5. Liquid Product Recovery. The solids free gases coming out of the dust filter (F-301) enter a 3 m long dual pipe heat exchanger (HE-401). This is an air-cooled specially designed heat exchanger designed in such a way that allows the heavier and more viscous compounds to drain along its walls. Downstream of the heat exchanger a liquid product stabilizer exists for the separation of the liquid and gaseous products. The

stabilizer consists of an oil reservoir at the bottom (D-402), a column packed with a demister pad in the middle, and a reflux condenser at the top (HE-403). The condenser is cooled by the liquid cooling bath, achieving a wall temperature below 0 °C. The process gas coming out of the stabilizer passes through a final condenser (D-407) and finally through a charcoal trap that removes light oil and heavier gas components from the gaseous stream. These two vessels are also cooled by means of a cooling medium (wall temperature below 0 °C). Finally, the process gas (consisting mostly of nitrogen and light cracked gases) passes through a pressure control valve (PV-401) that maintains the pressure in the unit and passes through a wet test meter (WTM-401) before being vented. Gas samples for gas chromatographic (GC) analysis are withdrawn from a point upstream from the wet test meter.

2.2. Process Development Unit Control. The process development unit is fully automated based on a special industrial computer control system. It utilizes PC-based automation with an industrial-scale input/output subsystem (Beckhoff) connected through a Profibus interface. The system is coordinated by FIX automation software configured and designed by CPERI. The operator interface comprises computer screens based on representations of the process flow sheet. The signals collected and the manipulated outputs include analog and digital inputs and outputs. The control system records and observes these values in real time and also maintains a digital record of unit operation.

2.3. Product Analysis. The gaseous pyrolysis products were measured using an HP 6890 GC, equipped with four columns (precolumn OV-101; columns Porapak N, Molecular Sieve 5A, and Rt-Qplot) and two detectors (TCD and FID). The solid product (char and coke) was analyzed, using an elemental (C and H) analyzer. For the physical characterization of bio-oil standard analytical techniques were applied, based on methods used for conventional fuels analysis. The chemical characterization of the bio-oil was performed based on GC and GC/mass spectrometry (MS) analytical techniques employed to the ether-soluble fraction of the bio-oil. For the GC analysis an HP 5890 GC, equipped with an HP-5 column and a FID detector, was used while for the GC/MS analysis an HP 5989 MS ENGINE (electron energy 70 eV; emission 300 V; helium flow rate 0.7 cm^3/min; column HP-5MS) was used.

2.4. Feed Material. A forestry residue biomass feed was used in this study in order to investigate the operation performance of the new unit. It originates from beech wood and its main properties are the following: C (wt %) 49.41, H (wt %) 6.73, N (wt %) 0.16, O (wt %) (by difference) 42.96, ash (wt %) 0.54, moisture (wt %) 8.25, Na (mg/kg) 43.8, K (mg/kg) 326, and gross heating value (GHV; MJ/kg) 18.22. The average particle size of the feeds was 658 μm, while the detailed particle size analysis showed $D(v,0.1)$ 164 μm, $D(v,0.5)$ 366 μm, and $D(v,0.9)$ 658 μm. A silica sand with particle size in the range 100−250 μm and bulk density = 1.56 g/mL was used as a solid heat carrier.

3. Results and Discussion

3.1. Unit Operation. For the unit operation the solid heat carrier and the biomass feed are initially loaded into the regenerator and the feed hopper, respectively. The regenerator is fluidized with nitrogen and is heated at a temperature 100−130 °C higher than the desired pyrolysis temperature. The biomass feed in the hopper is kept at ambient temperature. The stripper, the cyclone, and the dust filter are heated at a constant temperature of 400 °C. The main independent operating variables of the unit are (i) the reactor temperature and (ii) the
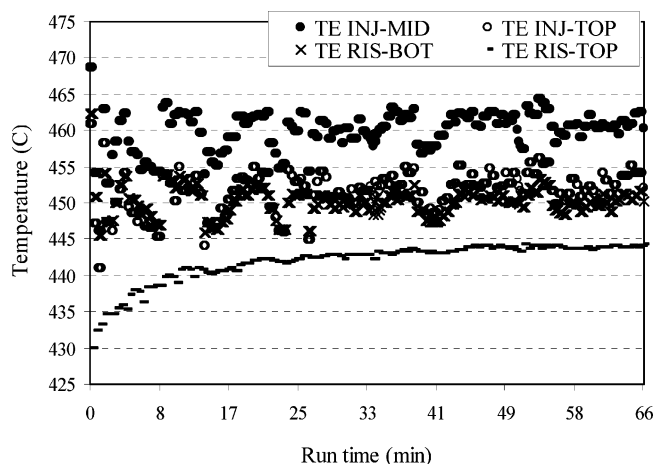

Figure 3. Temperature profiles during an experimental run. Based on explanation provided in Figure 2: TE INJ-MID:TE-202B; TE INJ-TOP: TE-202A; TE RIS-BOT:TE-203A; TE RIS-TOP:TE-203C.

temperature of the regenerator. The reactor temperature is considered to be the pyrolysis temperature and is measured as the temperature of the riser bottom (TE-203A in Figure 2). This temperature controls the opening of the regenerator slide valve. For a constant biomass feed rate and pyrolysis temperature, the regenerator temperature controls the solid circulation and thus the solid-to-biomass ratio (S/B). The experimental runs in this unit normally last for about 1 h. Liquid products are collected at the end of the run from the bottom of the stabilizer (D-402) and the condenser located downstream (D-407). These two liquid samples are mixed, both chemical and physical analyses are performed, and the blend is the final total bio-oil in which all analytical measurements are performed. At the end of the experiment the spent solids are loaded manually into the regenerator and heated at 680 °C with air, as fluidization gas, for regeneration.

3.2. Unit Stability. As already been mentioned, the reactor temperature is the most important variable in the pyrolysis process, and thus, it needs careful control. For a typical experiment at 450 °C the temperature profile of the injector and riser is depicted in Figure 3. The initial time ($t = 0$) is defined as the moment that the biomass feed is introduced into the reactor. The riser bottom temperature is considered to be the pyrolysis temperature, and is used to control the regenerator slide valve. Its deviation from the set point is ±3 °C. The maximum temperature is recorded at the injector middle, where intimate contact of hot regenerated solid and biomass takes place. At the top of the riser, the minimum temperature is observed due to the endothermicity of the pyrolysis reactions. The temperature difference between the different parts of the reactor from the average reactor or injector temperature is less than ±10 °C, while about 8 min is required to stabilize the temperature at the riser top.

A large number of tests (>60) have been performed in the unit under a wide range of operating conditions ($T = 450−550$ °C, S/B = 10−30) using different types of solid materials (inert and catalytic). During all these tests the stability of the unit was satisfactory and no operating problems were encountered. The process mass balances achieved for a significant number of experiments are given in Figure 4. With the exception of some preliminary runs where the mass balances were below 90 wt %, in all other runs the mass balances were above 92 wt %. This mass balance closure is considered satisfactory for biomass pyrolysis systems.[12]

3.3. Biomass Pyrolysis Results. 3.3.1. Product Yields. The total liquid product yields obtained from the present experi-
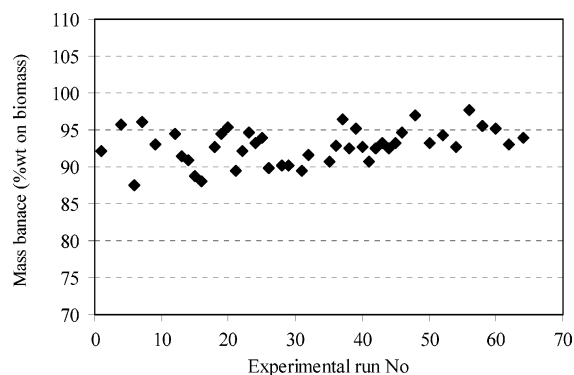
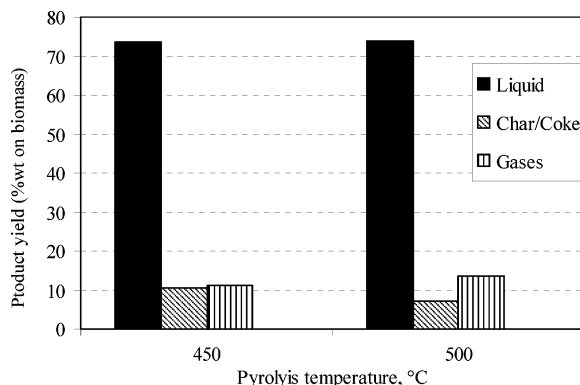**Figure 4.** Raw mass balances vs experimental run number.

Figure 5. Product yields as a function of pyrolysis temperature.

mental system, using silica sand as the heat carrier, were in the range 65−78 wt % (on biomass feed basis) depending on the experimental conditions. In Figure 5 the raw total liquid yields at two pyrolysis temperatures (450 and 500 °C) are presented. A constant S/B ratio of 16 was used for the two experiments. At both temperatures the liquid yields are very high (at the level of 74 wt %), with that at 500 °C slightly higher (about 0.5 wt %). This comes in accordance with published data,[12] and it seems that there is a maximum in bio-oil yield in the range of 450−500 °C. However, taking into account experimental errors, it seems that there is almost a plateau in bio-oil yield within this range of temperatures. This plateau was also pointed out by other researchers.[12,25]

Raw liquid yields around 75 wt % are among the highest reported in the literature for fluid bed pyrolysis units.[2,3,12,25,26] The liquid yields produced in the present system are comparable with the yields obtained by the work of Freel et al.,[10] where a similar transported unit and also silica sand as the heat carrier were used. Compared to our previous experimental system,[24] the present one produces about 10 wt % higher liquid yields using the same feed and heat carrier. The higher liquid yields achieved from the current unit can be attributed to four reasons: (i) The first reason is the new design of the mixing zone that assures a very rapid mixing of biomass particles with the hot sand particles that come from the regenerator. This hot sand enhances the heat transfer because of its higher heat capacity and its ability to mechanically ablate the surface of the reacting biomass. Based on the theoretical estimation of the biomass residence time in the mixing zone and on the temperatures measured by the thermocouples in this zone, it is concluded that the biomass feedstock heating rate in the present system is above 1000 °C/s. (ii) The higher liquid yields are also due to the presence of sand in the riser reactor (where most of the secondary reactions occur) in high circulation rates, which diminishes any catalytic effect of the remaining char, and (iii)
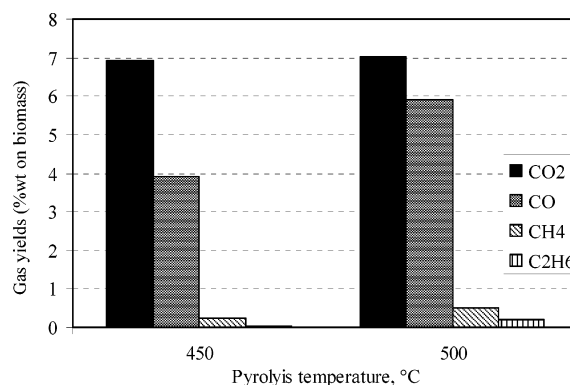

Figure 6. Gas yields as a function of pyrolysis temperature.

the residence time of the vapor in the riser, which is very low (<1 s) due to the nitrogen used for the fluidization and due to the high volume of the vapors produced from the pyrolysis in the mixing zone. (iv) The fast separation of solid and vapors in the cyclone type stripper and the fast quench of the produced vapors in the heat exchangers result in higher liquid yields.

In Figure 5 the yields of the other pyrolysis products are presented. At 450 °C both total gas and char yields are about 11 wt %. However, by increasing the temperature, the gas yield increases while the char yield decreases. The increase of the total gases following an increase in temperature is attributed to the higher conversion rates of primary pyrolysis reactions (resulting in lower char yield as observed in Figure 5) and not in secondary cracking reactions. If the secondary reactions were favored, then more char/coke would be produced together with less liquid yield. Consequently, it is concluded that in the present experimental system (with vapor residence time around 1 s) the secondary reactions are insignificant.[25] In the pyrolysis gases the oxygen compounds (CO, CO_2) dominate (Figure 6). Concerning the remaining gases, some light hydrocarbons were detected in very limited amounts (mainly CH_4 and C_2H_6 with yields less than 0.5 wt % on biomass basis). At 450 °C the CO_2 was the component with the highest yield (6.9 wt % on biomass basis) while CO was the second one with yield at 3.8 wt %. However, by increasing the temperature even for 50 °C, the CO_2 remains the same, while the CO increases rapidly, reaching yields around 6 wt % at 500 °C. This is because mostly CO_2 is produced by carboxyl groups which can be easily decomposed at relatively low temperatures. On the contrary, CO is formed by cracking of the most stable carbonyl groups and, thus, higher temperatures are required for higher productions.[2,27] All our results regarding the effect of temperature on product yields are in agreement with results reported in the literature.[2,25,26]

3.3.2. Bio-oil Quality. The water content of bio-oil at 450°C was 24 wt %, while at 500 °C it was slightly lower (22.6 wt %). In both temperatures the bio-oil was of a single phase. In the literature a wide range of water content in bio-oils has been reported (15−30 wt %), depending on the type of feedstock and process conditions.[3,6,9] The water in bio-oil originates both from the original moisture in the feedstock and from the primary dehydration reactions occurring during pyrolysis.[6] In our experimental system the difference of the water content in bio-oil between the two temperatures is relatively low. In the literature[25] it was reported that the water content in bio-oil comes through a minimum at about 500 °C, while after this temperature water production increases significantly due to secondary cracking reactions. Water is one of the main products of secondary cracking reactions (in case they are favored).[25]

The GC/MS analysis of the ether-soluble bio-oil fraction showed the existence of several hundred distinct organic compounds at detectable quantities including hydrocarbons, acids, aldehydes, ketones, phenols, furans, ethers, alcohols, and other compounds containing more than one of the above-mentioned functional groups. The quantitative analysis (by GC/MS[28]) of the ether-soluble fraction of the bio-oil showed that the bio-oil contained mainly phenolic and carbonylic compounds (about 5.8 and 4.0 wt %, respectively). Furans, acids, and hydrocarbons were about 2.5 wt % each. Moreover, the heavy oxygenates and the unidentified compounds were found in significant amounts (14.7 and 9.7 wt %, respectively). It must be pointed out that the effect of temperature (from 450 to 500 °C) on bio-oil quality was not important. Regarding the physical properties of the bio-oil produced in the current experimental system, they were within the ranges reported in the literature.[6,9,29] The density of the bio-oil was 1.19 g/cm^3, while the micro carbon residue (MCRT) was relatively high due to the presence of the heavy oxygenated components. The presence of water in the bio-oil is responsible for the low calorific value (GHV) of this product (16.3 MJ/kg). Taking into account that the bio-oil is 74 wt % of the biomass, it seems that about 66% of the initial biomass energy is transferred to the bio-oil.

4. Conclusions

A new fully automated process development unit has been designed and constructed at CPERI for biomass fast pyrolysis, based on the concept of transported fluid bed technology. The process development unit demonstrated excellent operating stability and flexibility and very satisfactory mass balances using different types of biomass. The experimental unit employed rapid mixing of biomass with the heat carrier medium, short residence time of the produced vapors in the riser reactor, and rapid vapor quenching in the product recovery section. These features resulted in the production of high liquid yields around 75 wt % (on biomass basis). The chemical and physical characteristics of bio-oil were measured by applying different analytical techniques and were found to be in agreement with the literature. Experiments with a woody biomass were performed at two temperatures (450 and 500 °C), which showed that the temperature change has a minor effect on liquid yield and quality. However, the temperature of 500 °C is more favorable, because at this temperature less char is produced with more CO in the light gases and less water in the bio-oil.

Acknowledgment

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