PRODUCTION AND CHARACTERISATION OF BIO-OIL FROM CATALYTIC BIOMASS PYROLYSIS

by

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Biomass flash pyrolysis is a very promising thermochemical process for the production of bio-fuels and/or chemicals. However, large-scale applications are still under careful consideration, because of the high bio-liquid upgrading cost. In this paper the production of bio-liquids from biomass flash pyrolysis in a single stage catalytic process is being investigated using a novel once through fluid bed reactor. This biomass pyrolysis unit was constructed in Chemical Process Engineering Research Institute and comprises of a catalyst regenerator, a biomass-vibrating hopper, a fluidization reactor (that consists of an injector and a riser reactor), a product stripper along with a hot cyclone and a filter housing and finally a product condensation/recovery section. The unit can process up to 20 g/min. of biomass (50-800 μm) and can circulate up to 300 g/min. of catalyst or inert material. The experiments performed in the pilot plant showed that the unit operates without problems and with satisfactory mass balances in a wide range of experimental conditions both in the absence and presence of catalyst. With the incorporation of an FCC catalyst in the pyrolysis, the physical properties of the bio-oil produced changed, while more stable bio-oil was produced.

Key words: *biomass, catalytic pyrolysis, bio-oil characterisation*

Introduction

Biomass flash pyrolysis (BFP) is the thermal decomposition of biomass at temperatures of 400-550 °C in an inert atmosphere (in the absence of oxygen) using high heating rates and short residence times for both solids and volatiles. Liquid yields up to 80 wt.% have been reported at mild operating conditions (500 °C, 1 atm). Moreover, useful gases can also be produced (depending on the conditions) from biomass pyrolysis. Both pyrolysis liquids and gases can be used for energy and power production. Moreover, liquid products can be used as transportation fuels after a hydrotreating upgrading. Several reactor configurations have been proposed in literature aiming in maximizing mainly the liquid yields. They include bubbling fluidized beds [1-5], ablative reactors [6-7], cyclonic reactors [8], circulating fluid beds (CFB) [9], and vacuum pyrolysers [10]. A detailed review of all biomass processes is given elsewhere [11].

The pyrolysis oils obtained from a pyrolysis process are considered to be very promising bio-fuels as they can be easily transported, be burnt directly in thermal power stations, be injected into a conventional petroleum refinery, burn in a gas turbine or upgraded to obtain a light hydrocarbon fuel [12]. A main problem when dealing with pyrolysis oil is its high amount of water and its instability because of the presence of organic compounds with undesirable properties. The flash pyrolysis oils (bio-oils) are acidic, viscous, reactive, and thermally unstable. Due to these properties many problems arise in their handling and utilization [13]. Therefore, some upgrading, *e. g.* catalytic conversion with or without hydrogen, is required. Various catalysts have been introduced in pyrolysis in order to improve the quality of the bio-oil produced. The catalytically produced oils present a series of improved properties, such as stability and deoxygenation, but the amounts produced are lower than in the non-catalytic runs. Lappas *et al.* in a previous study [14] have suggested that the stability of the bio-oil depends on the pyrolysis experimental conditions (T – temperature, S/B – solid to biomass ratio) and the catalyst type and activity. Nokkosmaki *et al.* [13] found that ZnO catalyst increased the stability of the produced bio-oils.

In this work some details of the construction and design of a pilot plant unit located at Chemical Process Engineering Research Institute (CPERI), which is based on the CFB technology, will be presented. In the past we performed some CFB pyrolysis tests using an existing fluid catalytic cracking unit [14]. Results both from non-catalytic and catalytic runs in terms of product yields and bio-oil properties are also presented in the current study.

Experimental

Experimental unit

The unit configuration (fig. 1) is divided into five sections, which are discussed in the followings.

Biomass feed. The biomass feed section consists of a 4 liters cylindrical hopper mounded on a screw feeder of variable speed. A pneumatic vibrator is attached on the feed hopper to aid solid particles flow. The biomass feed is loaded into the feed hopper and is being fed into the reactor mixing zone (injector) using the screw feeder.

Solids feed. The solids feed system consists mainly of a 30 liters regenerator, two knockout drums, a filter, a heat exchanger, a slide valve, and a pressure control valve. The solids (catalyst or sand) are loaded manually into the regenerator while a differential pressure cell monitors the solids inventory in the vessel. The vessel is heated externally by controlled wall heaters (maximum temperature 815 ºC). Additionally, a multiple point well thermocouple is used to determine the internal temperature profile of the vessel inventory. The purpose of the regenerator (referred also as heat carrier vessel) is dual, first to regenerate the spent solids that have been used in a previous experimental run and second to supply to the solids the heat required for biomass pyrolysis.

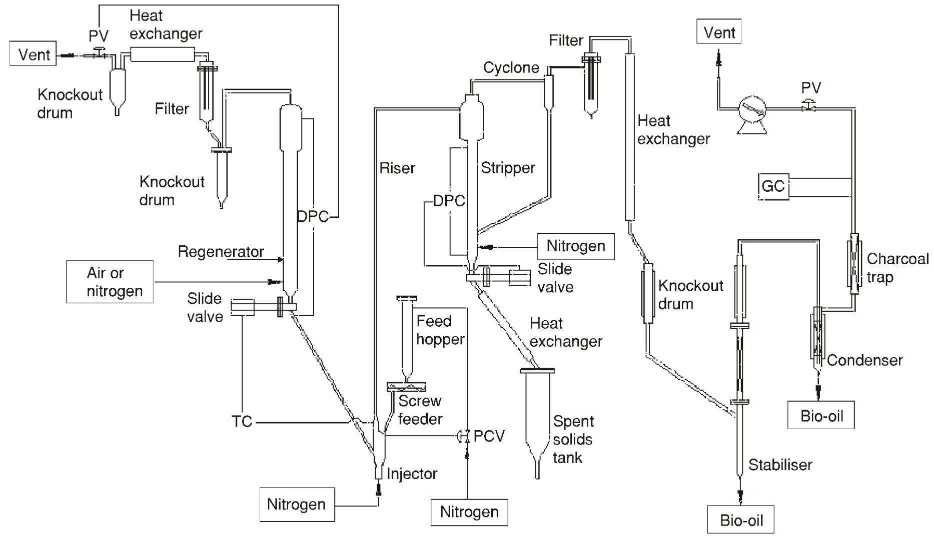

Figure 1. Pilot plant overview

PV – pressure valve, DPC – differential pressure controller, GC – gas chromatography, TC – temperature controller, PVC – pressure control valve

Reactor. The reactor consists of the injector and the riser. The injector is designed to promote the mixing of the hot solids (catalyst or sand) with the biomass particles. In addition, a stream of hot fluidization nitrogen is introduced from the bottom of the injector to transport the solids mixture into the riser, an almost five meters long vertical tube of 6,2 mm internal diameter. Pyrolysis reactions initiate in the injector and then continue into the riser. Several thermocouples have been installed to measure the internal temperature of both injector and riser. In addition, wall heaters that supply part of the heat required for pyrolysis cover both vessels.

Stripper and solids recovery. Gases and solids leaving riser, enter tangentially into the cyclonic head of the stripper that allows solids removal. Collected solids form a bed of fluidized material since hot nitrogen is blown from the bottom of the stripper. Trapped vapors within solids bed are carried along with fluidization nitrogen and escape from the top of the vessel. Gases along with some fine particles leaving from the top of the stripper enter a hot cyclone. Removed solids there return to the stripper through a heated transfer line. Gases are further filtered through a hot filter of 5 μm before moving into the liquid product recovery section.

Liquid product recovery. The solids free gases coming out of the dust filter enter a three meters long single pipe heat exchanger. This is an air-cooled vertical heat exchanger that allows the heavier and more viscous compounds to drain along its walls. Downstream heat exchanger is located a water-cooled knockout drum and further downstream a product stabilizer. These two vessels are also cooled by a circulating mixture of glycol and water (wall temperature –10 °C). Gas samples for GC analysis can be withdrawn from a point downstream the charcoal trap.

Pilot plant automatic control. The pilot plant is fully automated based on a special industrial computer control system. It utilizes PC-based automation with industrial scale I/O subsystem (Beckhoff) connected through Profibus interface. The system is coordinated by FIX automation software configured and designed by CPERI.

Product analysis

The gaseous pyrolysis products are analyzed 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 & coke) is analyzed using a LECO analyzer. Special emphasis is given on the analysis and characterization of the liquids products. For their physical characterization a wide range of standard analytical techniques are applied (based on conventional fuels) namely: ASTM 4052 (density), ASTM D1744 (H_2O), ASTM D445 (viscosity at 50 ºC), ASTM D4530 (MCRT), ASTM D97 (pour point), ASTM D93 (flash point), and ASTM D4809 (calorific value). For the chemical characterization of the ether soluble fraction of bio-oil the GC and GC/MS analytical techniques are employed. For the GC analysis was used an HP 5890 GC equipped with an HP-5 column and a FID detector to measure 34 selected organic compounds that fall within the group of phenols, carbonyls, and aromatic hydrocarbons. For the GC/MS analysis an HP 5989 MS ENGINE is used (electron energy 70 eV; emission 300 V; helium flow rate: 0.7 cm^3/min.; column: HP-5MS) and a detailed qualitative analysis of bio-oil is performed.

Biomass feedstock

A forestry residue (beech wood) sawdust (Lignocell HBS150/500 by Rettenmaier GmbH) has been used as biomass feed. The elemental analysis (%wt. on dry basis) and the particle size distribution for the beech wood under study is: C = 49.41, H = 6.73, O = 42.96, N = 0.16, Ash = 0.54, Na = 0.0044, K = 0.0326, and D(v, 0.1) = 164 μm, D(v, 0.5) = 366 μm, D(v, 0.9) = 658 μm.

Solid heat carrier

As heat carrier medium for the non-catalytic experiments was used silica sand (particle size range: 100-250 μm, bulk density: 1.56 g/ml) while for the catalytic an equilibrium FCC catalyst (particle size range: 50-180 μm, bulk density: 0.96 g/ml, TSA: 178.4 m^2/g, ZA: 58.5 m^2/g, UCS: 24.26 Å, Ni: 150 ppm, V: 367 ppm).

Unit specifications

The unit specifications are summarized in tab. 1.

Table 1. Pilot plant specifications

Unit parameter	Operating range
Regenerator temperature, [ºC]	<680
Reactor temperature, [ºC]	450-550
Reactor pressure, [atm]	1.7-3.0
Regenerator capacity, [l]	<30
Solids rate, [g/min.]	100-300
Feed hopper capacity, [l]	<3
Biomass feed rate, [ml/min.]	30-60
Biomass particle size range, [μm]	50-800
Vapor residence time in tiser, [s]	<1

Experimental results and discussion

Unit operation

The solid heat carrier (catalyst or sand) and the biomass feed are loaded into the regenerator and feed hopper, respectively. The regenerator is fluidized with nitrogen and it is heated at a temperature of 100-130 °C higher than the desired (for the test) reactor temperature. Biomass in the hopper is kept at ambient temperature. The stripper, the cyclone and the dust filter are always heated at a constant temperature of 400 °C. The reactor pressure during the experiment is normally close to 20 psig while the regenerator and the biomass feed hopper pressure is 2 psig higher. The main independent operating variables of the unit are: (1) the reactor temperature which is adjusted at a certain predetermined value; this temperature is considered to be the pyrolysis temperature and it is defined as the temperature of the riser bottom, and controls the opening of the regenerator slide valve, and (2) the temperature of the regenerator; for a constant biomass feed rate and pyrolysis temperature this temperature controls the solid circulation and thus the solid to biomass ratio (S/B).

Once the unit has been prepared for the selected experimental conditions and a steady catalyst flow has been established, the experimental run commences by introducing a steady biomass flow. The run time depends on the solid circulation rate since at the end of the run all solid from the regenerators passes to the stripper. Experimental runs normally last for about one hour. In certain time intervals during the experiment, gas samples are collected for GC analysis. Liquid products are collected at the end of the run from the bottom of the stabilizer and the condenser located downstream (fig. 1). The charcoal trap is also removed and weighted. Solids collected in the spent solids tank are allowed to cool down before sampling. Spent solids are also collected from the hot filter downstream stripper, normally <1% of the total solids. Several representative samples of spent solids are taken and sent for carbon analysis along with some blank samples of regenerated solids. 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.

Reactor temperature is the most important variable for the pyrolysis process and thus, it needs careful control. The biomass feed is introduced on time = 0 min. The riser bottom temperature is considered as the pyrolysis temperature, and is used to control the regenerator slide valve. Its deviation from the set point is 3 °C. The maximum temperature appears at the injector middle, where intimate contact of hot regenerated solid and biomass takes place. The minimum temperature appears at the riser top due to the endothermicity of the pyrolysis reactions. The temperature deviation, within injector and riser, from the average reactor temperature is 10 °C or less and takes about 8 min. to reach equilibrium.

Till today a large number of tests (>60) have been performed in the unit for a wide range of operating conditions (*T* = 450 – 550 °C, S/B = 10-30) using different types of solids (sand and catalysts) and the two types of biomass (forestry residue and energy crop). In all these tests the stability of the unit was satisfactory and no serious operating problems have been encountered. The process mass balances achieved for a significant number of experiments are given in fig. 2.

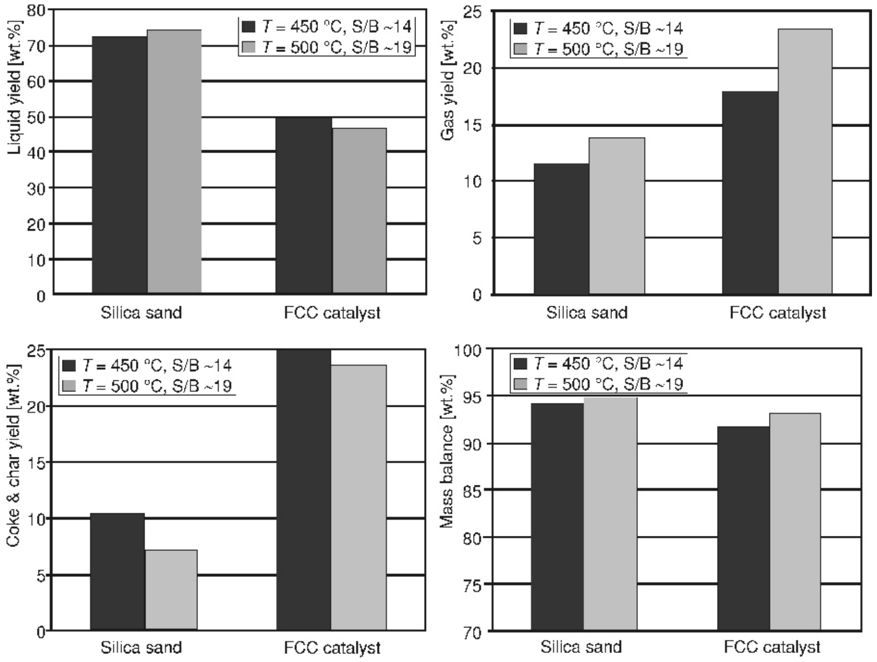

Figure 2. Average product yields and mass balances obtained for both catalytic and non-catalytic experiments

Catalyst effects in product yields

The bio-oil produced from the conventional pyrolysis processes contains a high oxygen and water content, a low heating value while its miscibility with petroleum fuels is negligible. Moreover, bio-oil is unstable under storage and heating conditions.

For this reason catalytic biomass pyrolysis could be a promising alternative for producing bio-oil of improved quality *in-situ* and thus eliminated the costly condensation/re-evaporation processes otherwise required for bio-oil upgrading processing. The CPERI circulating fluid bed unit can be effectively applied to catalytic biomass pyrolysis since it is very flexible to work with different (inert or catalytic) heat carriers. Till today a series of catalytic and non-catalytic experiments have been performed within a range of reaction temperatures. For the non-catalytic experiments silica sand has been used while for the catalytic several different types of catalysts have been tested. In fig. 2 the average products yields are given from the pyrolysis of beech wood along with silica sand or FCC catalyst, at two different reaction temperatures (450 and 500 °C). This figure indicates that the FCC catalyst strongly favors the secondary reactions that lead to tar decomposition. Liquid production decreases while that of gases and coke&char increases considerably when the FCC catalyst is used instead of silica sand. On the other hand when the reaction temperature increases so does the gas production at the expense of coke&char production.

Catalyst effects in bio-oil quality

Catalysts, however, radically affect the bio-oil characteristics apart of its yield. The behaviour of bio-oil as a fuel is described in figs. 3 and 4. It appears that catalysts reduce the heating value of bio-oil and also reduce the flash point, the density and the viscosity. This is because of the presence of increased amounts of water and lighter organic compounds in the catalytic bio-oil due to cracking. The decrease is more significant in the temperature of 500 ºC, but only in the presence of the catalyst and this can be attributed to a more extensive cracking in a higher temperature in catalytic pyrolysis. The increased amount of water in the catalytically produced bio-oil was the reason why it could not be measured in the temperature of 500 °C. The change of viscosity of bio-oil has been also been suggested as an indicator of its thermal stability [15-16]. As it has already been mentioned, bio-oils are highly unstable and they start to polymerize even at ambient temperature with a resulting increase in the viscosity. Both non-catalytic and catalytic bio-oils were aged at 80 °C for 24 h in order to study their stability. It appears from fig. 4 that the catalytically produced bio-oil is quite stable in contrast to the non-catalytic one. It was concluded during the research that when the FCC catalyst is incorporated in the pyrolysis the bio-oil produced, it demonstrates very good thermal stability in comparison to the non-catalytic, mainly due to the inhibition of the thermal polymerization on the bio-oil components with the presence of the catalyst.

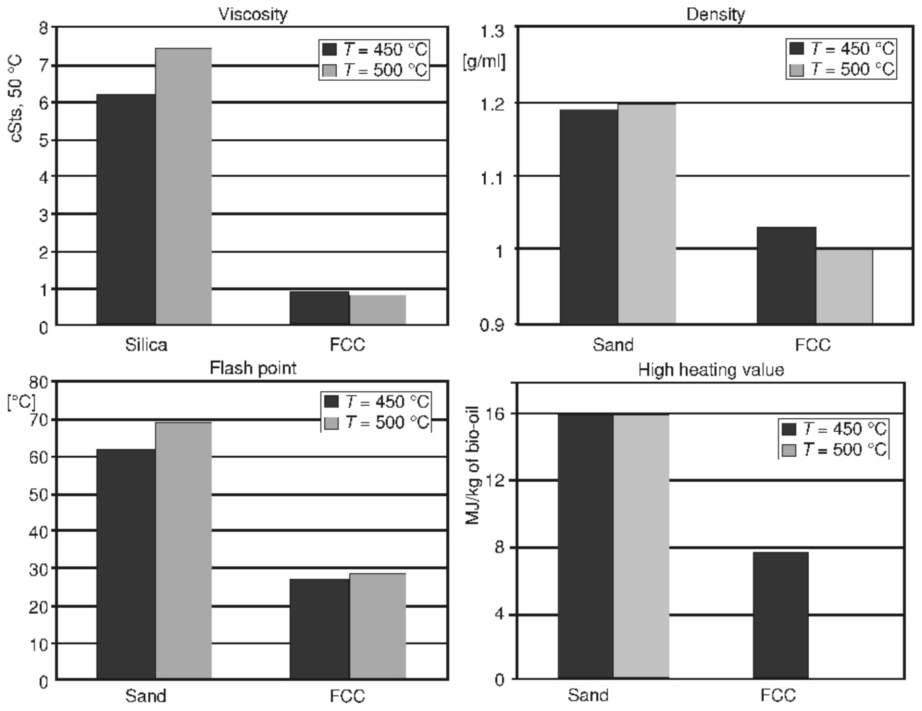

Figure 3. Viscosity, density, flash point, and high heating value of bio-oil

However, the catalytically produced bio-oil has lower heating value and allows phase separation on storage. Yet phase separation may be desirable in order to acquire a layer condensed in organics and low in water that has considerably high heating value, while the remaining dilute phase that contains water soluble organic compounds, such as acetic acid, may be further treated to recover these chemicals.

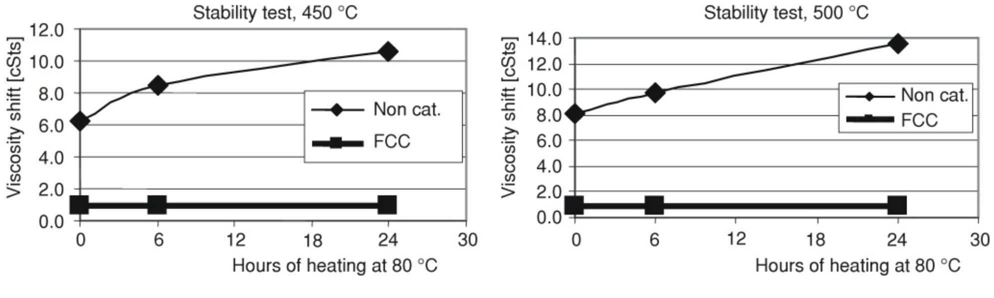

Figure 4. Thermal stability of bio-oil

Conclusions

A fully automated pilot plant unit for biomass pyrolysis has been constructed at CPERI based on the concept of circulating fluid bed technology. The pilot plant unit demonstrated good operating stability and flexibility with different types of biomass and heat carriers. The experimental unit employs 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. Both catalytic and non-catalytic experiments were performed. High liquid yields (up to 75 wt.%) have been achieved that are typical of flash pyrolysis reactors. The type of solid heat carrier seems to play a very important role in products yields and characteristics. With the use of the FCC catalyst instead of silica sand, liquid production decreases while gases and coke&char production increases. The main physical properties of the bio-oil, such as density, heating value, flash point and viscosity deteriorated in the presence of catalyst, mainly due to the high amount of water produced. However, promising results were obtained from the stability tests of the FCC produced pyrolysis oil.

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