Formation of Liquid and Solid Products of Liquid Phase Pyrolysis

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Abstract:

Lignocellulosic feed is expected to contribute significantly to production of liquified and solid combustibles. Aim of this project is the production of high quality biochar and a liquid energy carrier. Therefore the pyrolytic degradation of softwood during liquid phase pyrolysis was investigated. The process was carried out in a semi-batch reaction vessel under isothermal conditions at various temperatures. Process pressure was ambient. For optimum heat transfer pyrolysis was carried out in liquid heat carrier phase which provides high heat conductivity. Liquid phase pyrolysis is an exothermic process which produces 25-28% liquid CHO products, independent of biomass particle size within a range of 630 µm and 10 mm. The enthalpy of reaction is -864±25 kJ/kg at T=350°C.

Keywords: liquid phase Pyrolysis, lignocellulosic feed

1 I. Introduction

30% of European Union energy consumption is needed for traffic and mobility and 98% of these fuels are from fossil sources [Biofuels Research Advisory 2006]. The European Union wants to reduce greenhouse gas emissions due to the European Directive 2009/28/EC by 20% and rise the percentage of renewable fuels up to 10% [EU-Directive 2009/28/EC (2009)]. This policy and the strategies for sustainability open a wide range for renewable resource fuels and combustibles all over the world. BtL (biomass to liquid) will play an important role in conversion of biomass to fuels and energy carriers. Thermo chemical conversion of biomass provides many applications in the value chain of fuels, electricity and chemicals [Bridgwater (2000)]. The number of different BtL processes in Germany [Behrendt (2006)] and all over the world [Bridgwater (2000)] is comparable with the variety of applications of BtL products [Bridgwater (1999)]. Different systems concerning biomass pre-treatment, product conditioning and collecting and reactor configuration are reported, different reactor systems have been investigated and proposed [Kaminsky (1989)].

Due to the avoidance of dust formation in the vapor phase and the high heat transfer rate during pyrolysis in liquid non aqueous heat carrier liquid phase pyrolysis neither needs high technical vapor biochar separation systems like in fluidized bed Pyrolysis [Mohan], nor does it need high pressure reaction atmosphere like hydrothermal carbonization [Bockhorn (2010)]. These are the reasons why liquid phase pyrolysis is following KISS principle (keep it smart and simple) enabling high potential in production of biochar and biocrudeoil [Witek (2009)].

2 II. Methods and Results

2.1 System

Liquid phase pyrolysis is performed in a fed-batch reactor vessel in an inert atmosphere shown in Figure 1. Liquid phase pyrolysis uses an alkane mixture with a boiling range between 400 and 500℃ as heat carrier. The liquid heat carrier provides high heat conductivity ~0.100 W/mK at T=350℃ and high heat capacity of ~2.4 kJ/(kgK) at T=350℃.

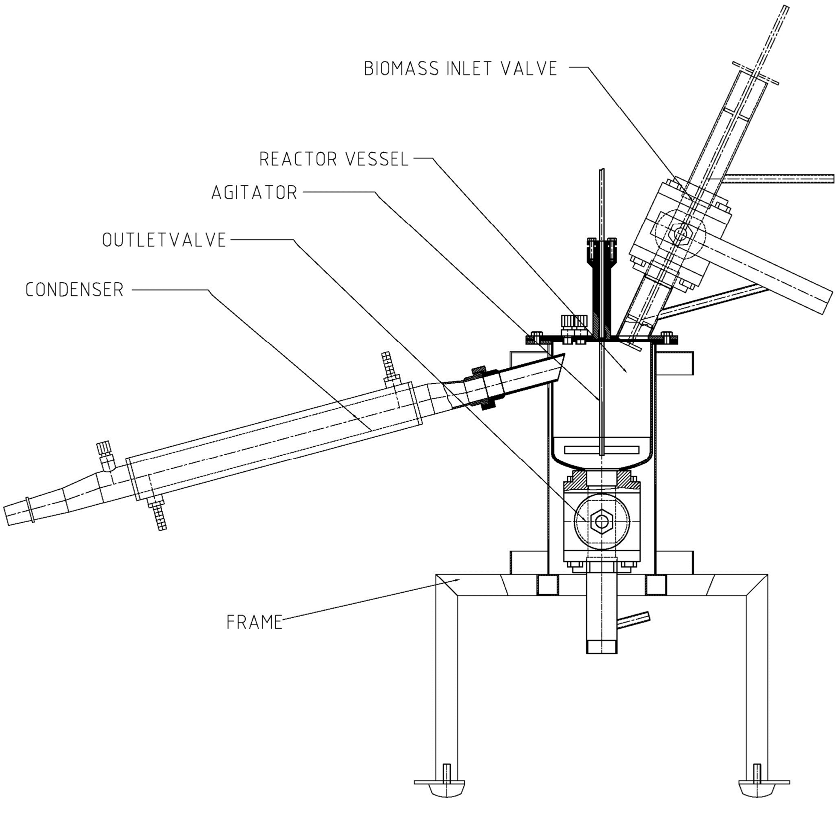

Figure 1: Schematic of liquid phase pyrolysis reactor vessel

2.2 Mass Balance and Products

Figure 2 shows the Biomass mass balance for T = 350℃. Three major product classes, gaseous, liquid and solid products are formed during pyrolysis. The non condensable gases are a mixture of about 33% of Carbon Monoxide, 51% Carbon Dioxide and volatile organic compounds with a major amount of methane. The solid product of liquid phase pyrolysis is biochar. The biochar has a carbon content of 75% and a lower calorific value of 27,3 MJ/kg. Biochar is separated from heat carrier by vacuum filtration or by evaporation at elevated temperature.

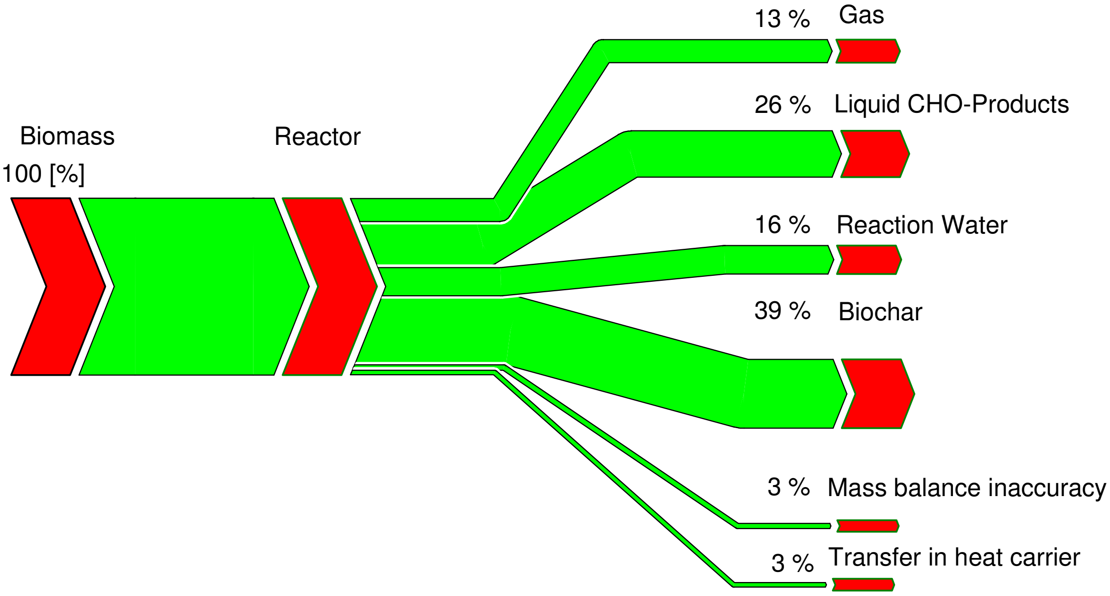

Figure 2: Mass balance at T= 350°C

The heat carrier cycle is shown in Figure 3. Through liquefaction liquid biogenous products, water and heat carrier form an azeotropic mixture. This causes loss of heat carrier with water and liquid CHO-Products. A minor part of heat carrier is degraded into condensable and noncondesable hydrocarbons. The non condensables are methane, ethane and various derivates of propane and butane. The condensable heat carrier degradation products are hydrocarbons.

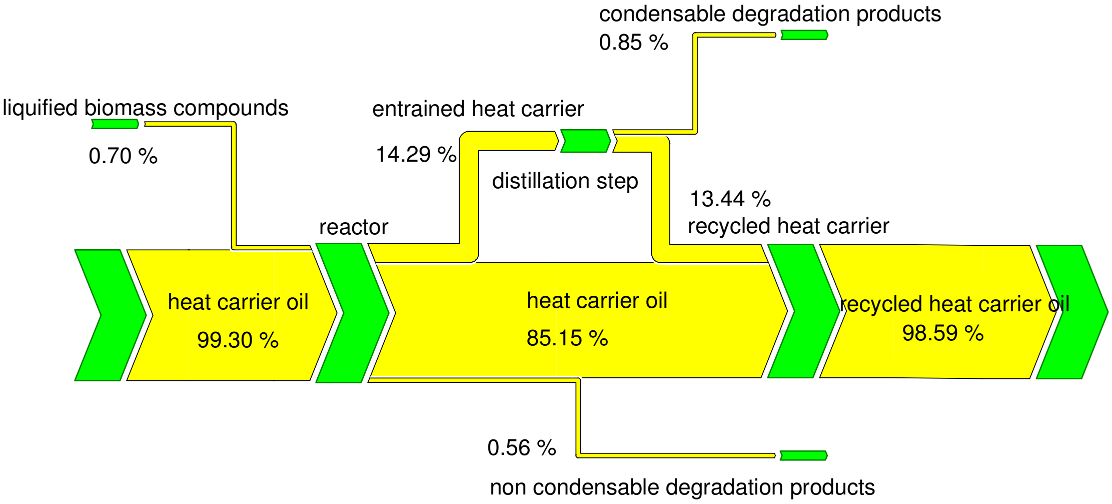

Figure 3: Heat carrier balance

About 3% of the biomass is transferred into the heat carrier oil during the whole liquefaction process, mainly composed of 2-Methyl-furane, 2,5-Dimethylfurane, 2-Methoxyphenol, 2-Methoxy-4-methylphenol, 4-Ethyl-2-methoxyphenol, 2-Methoxy-4-(2-propenyl)-phenol, 2-Methoxy-4-propylphenol, 2-Methoxy-4-(1-propenyl)-phenol.

2.3 Liquid Products

The main liquid products are water formed by reaction, and liquid CHO-products. 20% of the liquid products are low molecular weight organic compounds with a molecular weight between 30 g/mol and 200g/mol. Organic matrix is a mixture of non-GC-MS detectable Compounds with a molecular weight between 400 and 1200 g/mol. The main GC-MS detectabel substance classes are acids, ketones, furanes, guajacoles, sugars and alcohols as shown in Figure 4.

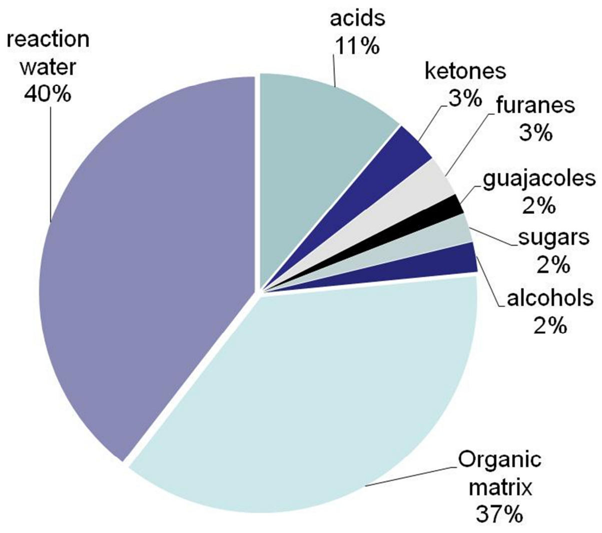

Figure 4: Liquid Products of liquid Phase Pyrolysis

Liquid-phase pyrolysis biocrude oil is “light biocrude oil”compared with flash pyrolysis biocrude oil [Meier (1999)] in Table 3. As a result of preferred biochar formation, less biomass is transferred into liquid products, explaining elevated water content and low carbon contents.

Table 1 Comparison between Liquidphase Pyroylsis Oil and Flash-Pyrolysis Oil

Parameter	Liquid Phase Pyrolysis	fluidized bed reactor (Meier, 1999)
Liquid Yield (wt%)	42	75
Water (%)	39	20
C (wt %)	31,5	55
H (wt %)	8,5	7
Heating Value MJ/kg	11,6	20

Biocrude oil from fluidized bed reactor pyrolysis is particle-loaded [Lédé (2007)], a major disadvantage which is not observed in liquid-phase pyrolysis. All liquid products are completely ethanol-soluble. Without separation steps for ash and char particles, biocrude oil from flash pyrolysis can carry up to 500 ppm sodium and potassium and up to 600 ppm calcium [12]. In liquid-phase pyrolysis particulate matter is trapped in the liquid heat carrier inside the reactor, the reason for low inorganic compounds in the unfiltered and untreated biocrude oil.

2.4 Thermodynamics and Product formation

With the upper calorific value (H_h) of all Products and Educts the enthalpy of fusion of all reaction participants [Westermeier (1986)] and the enthalpy of reaction was determined. The enthalpy of reaction for liquid phase pyrolysis of lignocellulosic feed is -864±25 kJ/kg at T=350℃.

To gain data about kinetics of formation of liquid and solid products degradation and product formation was recorded as shown in Figure 5. The solid line shows that formation of liquid products passes two distinct phases, exponential first dewatering phase and a linear product formation phase.

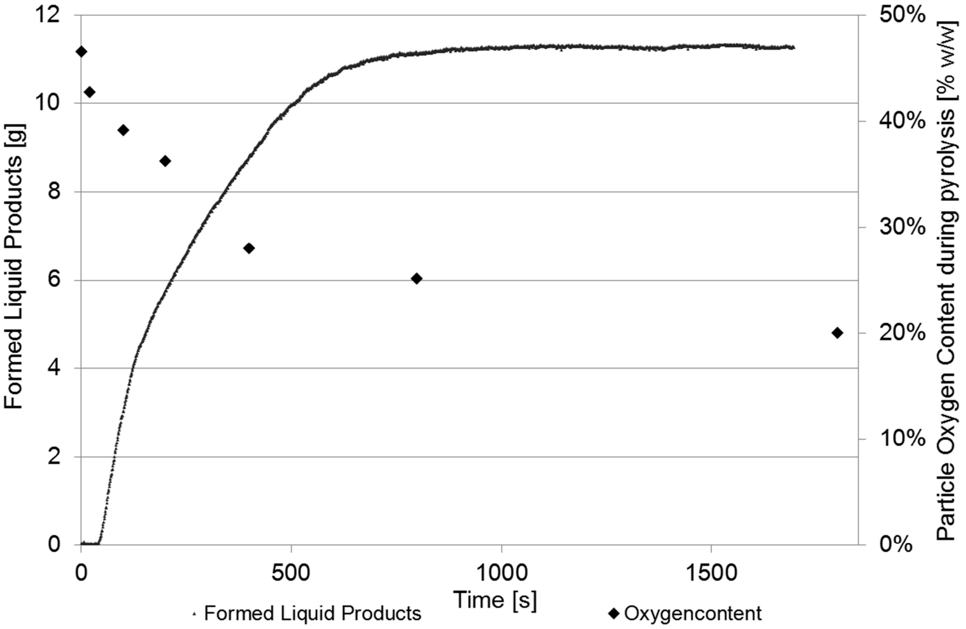

Figure 5: Formation of liquid and solid Products during liquid phase pyrolysis at T = 350 ℃ and ambient pressure

The dots show deoxygenation of lignocellulosic biomass. After a rapid loss of oxygen slow carbonization of the solid residues is observed.

2.5 Outlook

Further steps for liquid phase pyrolysis products are biochar hydrogenation and biocrude oil deoxigenation for liquid fuel production. Investigations are carried out in two batch reactors. One reactor has a volume of 1100 ml and can be operated at a maximum temperature of 400℃ and a maximum pressure of 20 MPa. The second reactor can be operated at a maximum temperature of 500℃ and 35 MPa and has a volume of 450 ml. First upgrading experiments showed very promising results.

3 References

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