

High quality bio-oil from catalytic flash pyrolysis of lignocellulosic biomass over alumina-supported sodium carbonate



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ABSTRACT

Performance of a novel alumina-supported sodium carbonate catalyst was studied to produce a valuable bio-oil from catalytic flash pyrolysis of lignocellulosic biomass. Post treatment of biomass pyrolysis vapor was investigated in a catalyst fixed bed reactor at the downstream of the pyrolysis reactor. In-situ catalytic upgrading of biomass pyrolysis vapor was conducted in an entrained flow pyrolysis reactor by feeding a premixed feedstock of the catalyst and biomass. $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ was very effective for de-oxygenation of the pyrolysis liquid and oxygen content of the bio-oil was decreased from 47.5 wt.% to 16.4 wt.%. An organic rich bio-oil was obtained with 5.8 wt.% water content and a higher heating value of 36.1 MJ/kg. Carboxylic acids were completely removed and the bio-oil had almost a neutral pH. This bio-oil of high calorific low, low water and oxygen content may be an attractive fuel precursor. In-situ catalytic upgrading of biomass pyrolysis vapor produced a very similar quality bio-oil compared to post treatment of pyrolysis vapors, and shows the possible application of $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ in a commercial type reactor system such as a fluidized bed reactor.

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1. Introduction

Pyrolysis-oil (hereinafter “bio-oil”) produced with current flash pyrolysis technologies is not suitable for direct use as a transportation fuel or as a fuel additive. The presence of oxygenated compounds in the bio-oil mainly contributes to its deleterious properties, high viscosity, non-volatility, high acidity and resulting corrosiveness and extreme instability upon storage, lower energy density than the conventional fuel by 50%, incompatibility and immiscibility with fossil fuels, thermal instability and tendency to polymerize under exposure to air [1–5]. Catalytic de-oxygenation is considered as a first line option to overcome the problem characteristics of the bio-oil beside catalytic reformation of the large lignin derived molecules into useful products.

The challenge in de-oxygenation catalyst development is to design a catalyst that selectively removes the problematic oxygenates in the bio-oil. The oxygen may be given off by de-hydration, de-carboxylation and de-carboxylation leading to the formation of water, CO and CO_2 , respectively. The de-carboxylation is the preferred route for de-oxygenation in comparison to de-hydration as de-carboxylation allows retention of hydrogen in bio-oil, maximizes oxygen removal with minimal carbon loss and thereby increases heating value, decreases the aromatic compounds, minimizes the water content of the bio-oil, and decreases

its hydrophilicity. Hence, in order to retain maximum energy content in the bio-oil, selective scission of bonds should follow the order of $\text{C}-\text{C} > \text{C}-\text{O} > \text{C}-\text{H}$.

So far, catalyst studies for biomass pyrolysis have been mainly focused on zeolites (Y, ZSM-5, mordenite and beta), and mesoporous aluminosilicates. However, zeolites and aluminosilicates have not shown any promising results. Major drawbacks to use relatively small pore zeolites are; a significant decrease in organic yield due to the increase of the production of water and gases, and a rapid catalyst deactivation by coke deposition [6]. Alkali metals are found to be effective catalysts for H_2O and CO_2 gasification of carbon [7]. Lee et al. used Na_2CO_3 for the catalytic gasification of rice straw over nickel catalyst and formation of gas was significantly enhanced [8]. The effect of alkali compounds on the properties of bio-oil has not been studied systematically and there is very limited literature available on the effect of alkali compounds on bio-oil. Several researchers [9–12] used alkali compounds as a catalyst for biomass pyrolysis and found that alkali compounds lowered the temperatures of biomass devolatilization and decreased biomass conversion time, these effects were enhanced by increasing the basicity of alkali compound and the use of Na with respect to the K ion. Bradbury et al. found that the inorganic content in the biomass has a significant effect on the yield of gas and char, and concluded that increasing the inorganic contents in the biomass promotes the secondary cracking reactions that leads to the breakdown of higher molecular compounds to smaller ones [13]. It is well known that cations of alkali metal in biomass can affect thermal decomposition mechanism of fast pyrolysis and can form the natural polymer chains

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via primary fragmentation of the monomers [14]. Raveendran et al. claimed that the alkaline cations have a significant effect on the catalytic pyrolysis of biomass compared to anion of alkali metals [15].

Alkali metals can be applied directly for catalytic biomass pyrolysis but direct addition of alkali metal catalysts has several disadvantages, e.g. difficult and expensive recovery of the catalyst. To solve these problems, they can be supported on a catalyst carrier e.g. alumina and taking advantage of catalytic effects of both alumina and alkali metal. Very few studies could be found on active alumina which is a solid acid catalyst [16,17]. Larger pore size alumina has potential for reducing the coke formation and enhancing the organic liquid yield due to their lower acidity. Larger molecules, particularly lignin-derived compounds, can enter, reformulate and exit the bigger pores of alumina with lesser chances of coke formation and resulting blockage of the pores. To take advantage of larger pore size alumina and alkali metal, a novel alumina-supported sodium carbonate ($\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$) catalyst is developed based on systematic studies at laboratory scale with batch experiments using a 2 g biomass sample and a catalyst fixed bed reactor [18]. In the current work, $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ has been implemented in a bench scale unit of 1 kg/h biomass capacity that consists of an entrained flow pyrolysis reactor. Post pyrolysis vapor treatment which was carried out in a catalytic fixed bed reactor to study the effect of the catalyst temperature independent of the pyrolysis reaction and to isolate the catalyst/vapor contact problems may occur in case of in-situ application of the catalyst in entrained flow pyrolysis reactor. In-situ upgrading of pyrolysis vapors was carried out in the entrained flow pyrolysis reactor with premixed feedstock of catalyst and biomass to simulate the condition of a commercial system such as fluidized bed reactor. The entrained flow downer reactor configuration is selected because of easy operation handling and it demonstrated high heating rates of the biomass while maintaining good control of the reaction conditions for instance the residence time of reactants and products [19,20].

2. Materials and methods

For the production of bio-oil via catalytic flash pyrolysis of woody biomass, a continuous bench scale unit of 1 kg/h feedstock (biomass/and catalyst) capacity has been designed. A schematic of the unit is presented in Fig. 1. The feedstock (biomass or biomass/catalyst) is loaded into the feed hopper and fed to the entrained down flow reactor by a screw feeder and inert carrier gas (nitrogen). The pyrolysis reactor is consisted of a cylindrical quartz tube of 4.2 m length with an

internal diameter of 5 cm. The reactor is heated electrically through heating coils around the wall and the reactor temperature is controlled by thermocouples installed at various heights of the reactor. Feedstock enters the reactor at its top, and in a few seconds the thermochemical conversion of biomass particles takes place under inert atmosphere yielding a gas composed of condensables (bio-oil), non-condensables, and char.

The catalyst fixed bed reactor was used only for the post treatment of pyrolysis vapor and it was bypassed for in-situ upgrading of pyrolysis vapor in an entrained flow reactor. The fixed bed reactor is made of stainless steel, 300 cm length and 6 cm internal diameter. The reactor is heated electrically and the catalyst is loaded before the start of the experiment. The vapor residence time in the catalyst fixed bed reactor is less than half a second.

The vapors, gases and solids leaving the reactor enter tangentially into a cyclone that allows removal of solid particles up to 20 μm . The solids consist of char (ash and unconverted biomass) for non-catalytic experiments and char plus spent catalyst for in-situ catalytic experiments. Due to a wide particle size distribution of the biomass and the catalyst, it is difficult to design a very efficient cyclone, therefore fine particles are separated in a hot filter element at the downstream of the cyclone. A solid free gas is carried to two double tube heat exchangers (operated with a coolant mixture of glycol and water at -5°C circulating through outer tubes). In this section the condensable fraction of the gases is recovered as a liquid. Heavy and middle fractions of the condensable vapors are recovered in the first condenser and lighter fraction of the bio-oil is recovered in the second condenser. The gases leaving the condensers still carry a mist or fumes of product vapors that are recovered in a rotating particle separator (RPS) where they are impinged onto the surface of filter and can flow downwards out of the filter by gravity as a liquid. The oil separated by the filter element is collected at the bottom of the RPS and taken off at the end of the test run. The RPS is very efficient to capture the mist of oil vapors and nearly vapor free gas leaves the RPS and is taken off for gas analysis. Other operating conditions and parameters are listed in Table 1.

2.1. Biomass

The biomass used for the experiments consisted of wood fibers commercially available with trade name Lignocel by J. Rettenmaier & Söhne GmbH. The biomass particle size varied from 0.1 to 1 mm. The ultimate and proximate analyses are presented in Table 2.

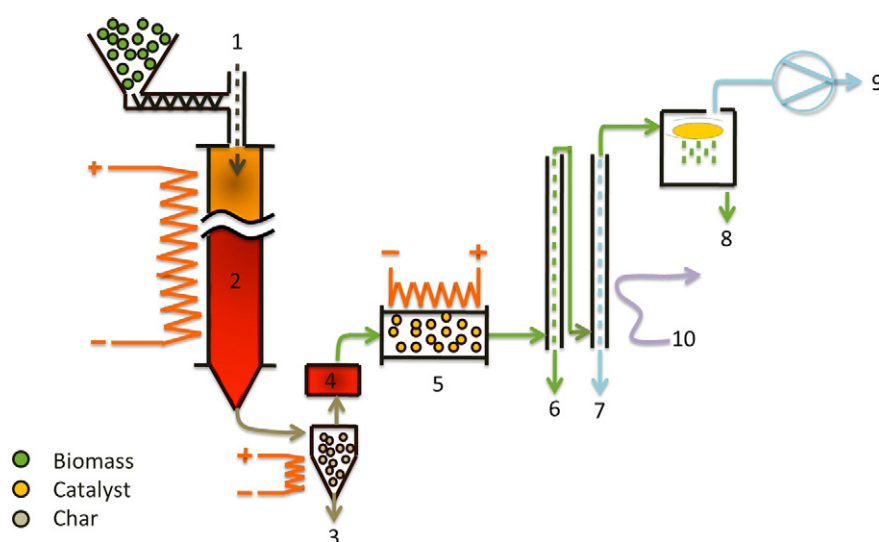


Fig. 1. Schematic presentation of the experimental setup. 1. Carrier gas (N_2). 2. Pyrolysis reactor. 3. Solid recovery. 4. Hot particle filter element. 5. Catalyst fixed bed reactor. 6–7–8. Liquid collection. 9. Gas to analysis unit. 10. Coolant.

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