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Liquefaction of lignocellulose: Do basic and acidic additives help out?

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HIGHLIGHTS

- Lignocellulose is liquefied with high liquid yield (~90 C%) in batch experiments.
- Use of base lowers the yield of undesired heavy product while acid increases it.
- Formation of heavy product is found dependent on pH of the liquid product.
- Base get partly neutralized and eventually favor the degradation of the bio-oil to heavy product under recycle conditions.
- Batch experiments are insufficient to evaluate acid/base additives.

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ABSTRACT

Lignocellulosic feedstock can be converted to bio-oil by direct liquefaction in a phenolic solvent such as guaiacol. The bio-oil could then be further upgraded to transportation fuel using conventional oil refining process. The production of heavy components (molecular weight >1000 Da) was found to be a major hurdle in this process as it hinders the efficiency of recycling the bio-oil as liquefaction medium. This paper studies the effect of bases and acids on the liquefaction of biomass and their effectiveness in reducing the formation of heavy components. Acid was found to have a negative effect while all the bases showed a positive effect in reducing the formation of heavy components. Production of heavy components was found to depend on the pH of the medium; it decreases with increasing pH of the product measured after the reaction. Both acid and base additives got partly neutralized during the reaction and, therefore, do not operate as true catalysts. Further refill runs with $KHCO_3$ were carried out to check the possibility to recycle the additive and the bio-oil as liquefaction medium. The additive appeared to perform poorly under recycle conditions. The base got neutralized and addition of fresh base catalyzed the degradation of the solvent (guaiacol) and the bio-oil upon oil recycling. This behavior may explain the recycling challenge faced in the PERC process. This study shows that single run experiments are insufficient to evaluate additives as they do not unravel acid/base deactivation and oil degradation. Refill runs are necessary for that.

1. Introduction

A variation of the pyrolysis for the production of bio-oil is the direct thermal liquefaction of lignocellulosic biomass under liquid phase conditions [1,2]. For instance, the PERC process [2–4] used Na_2CO_3 with reducing gas (CO/H_2). The PERC process failed due to serious technical problems caused by undissolved solids and an increase of medium viscosity [2]. The LBL process [5] developed later also used Na_2CO_3 with reducing gas (CO) and water as solvent. This process also ran into plugging problems.

Direct liquefaction of lignocellulosic biomass was also studied in detailed using various solvents in our group [6] and confirmed the potential of phenolic solvent such as guaiacol. Since guaiacol and its derivatives can be produced from the biomass, this opens up the possibility to use a fraction of the resulting bio-oil as reaction medium. The recycling of the bio-oil initially succeeded in achieving high oil yield but readily lost its effectiveness as the liquid medium became very viscous because of increasing formation of heavy product [6]. Further optimization of process

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Abbreviations: Da, Dalton; GPC, gel permeable chromatography; $M_{W,GPC}$, molecular weight defined by GPC; M_W, molecular weight; RID, refractive index detector; *T*, temperature; VR, vacuum residue.

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parameters had limited effect on minimizing the formation of high molecular weight compounds [7]. So there is a need for exploring other options such as the use of additives.

In the recent literature, much work has been devoted to the use of additives in the liquefaction and many of them have reported positive effect based on a single (batch) experiment [8–11]. However, such additives were also used under recycle operation in the PERC and LBL process and did not seem to be effective then.

The present work is therefore revisiting the potential of various base and acid additives to reduce the formation of heavy product in single runs and in recycle runs to explore eventual recyclability of the additive and the resulting bio-oil. The liquefaction was done with guaiacol and with small amount of water but without reducing gas. Reducing gas was avoided to keep the liquefaction reactor at moderate pressure and, thereby, minimize the technical challenge of feeding the solid biomass into the reactor and improving the economics of the process.

2. Materials and methods

2.1. Materials

Pine wood was obtained from Rettenmaier & Sohne GmbH (Germany). It was crushed to the particle size of <0.5 mm and then was dried at 105 °C for 24 h in an oven. The composition of the pine wood is provided in Supplementary information available. All other chemicals were obtained from Sigma Aldrich with a purity >98%.

2.2. Experimental setup and procedure

Experiments were carried out in two different batch autoclaves having internal volumes of 9 mL and 45 mL. These autoclaves were designed and build in-house with very thin walls to allow very fast heating rate (~300 °C in the 9 mL autoclave). Safe operation was then achieved by operating them in a high pressure room with external controlling of the unit. Autoclaves were mounted on the arm of a robot and all control could be done from outside the high pressure room. Screening of various bases and acids was done in the 9 mL autoclave while refill experiments were done in the 45 mL autoclave. The experimental set-up of both reactors and experimental procedure of the 9 mL reactor are described in detail elsewhere [7].

The experimental procedure for the refill runs was as follows: the feed charge was prepared by mixing the target amount of wood, water, guaiacol and additive. The additive was added after dissolution in the desired amount of water. The feed solution was mixed thoroughly, loaded into the 45 mL reactor. The reactor was closed tightly, flushed with nitrogen several times to remove any oxygen present in the system and pressurized to about 5 bar of nitrogen. Autoclave is mounted on the arm of a robot and all control can be done from outside the bunker. The stirrer was turned on and the autoclave was immersed into the preheated fluidized sand bed which had a temperature of around 5 °C higher than the desired reaction temperature. After the desired reaction time, the reactor was lifted off the sand bath and quenched in a cold water bath. The autoclave was subsequently cooled to ambient temperature and the gas sample was taken using a syringe. After depressurizing, the autoclave was then opened and a small amount of sample was taken out (normally 1 g) for the analysis. The remaining liquid (with eventual suspended solid) was used as a liquid solvent for the subsequent run. Subsequently a second weighted amount of dry pine wood mixed with a second weighted amount of water with/without additive was added to the autoclave and the autoclave was sealed and subjected to a second run. At the end of the refill runs, the remaining product (liquid and solids in suspension) was then collected in a glass vial and the reactor was rinsed with acetone to remove leftover liquid and solid deposits. The obtained acetone wash was filtered with filter paper of size 1.6 μm. The obtained product slurry (liquid + solid) was also filtered with a filter of pore size 1.6 μm, when necessary after dilution in some acetone to lower its viscosity. The obtained solid was dried at 105 °C and atmospheric pressure. In case of liquefaction with $KHCO_3$, the solid was further washed with water (to ensure removal of $KHCO_3$) followed by acetone before drying at 105 °C.

The reaction temperature was defined as being the end temperature and reaction time was defined as being the time that the autoclave spent in the hot sand bath.

Gas samples were analyzed with an off-line gas chromatography (Varian Micro GC CP-4900 with two analytical columns, 10 m Molsieve 5A and 10 m PPQ, using Helium as carrier gas). Gas chromatography–mass spectrometry (GC/MS) analysis was performed with an Agilent GC/MS (GC 7890A MS 5975C) to identify the compounds present in the liquid after the reaction. The liquid product was analyzed with Gel Permeation Chromatography (GPC) (Agilent 1200 series, with RI and UV (wavelength: 254 nm) detectors), using 3 GPC PLgel 3 μm MIXED-E columns connected in series. The column was operated at 40 °C with tetrahydrofuran (THF) as solvent. Apparent molecular weights ($M_{W,GPC}$) were determined by calibration with a solution of polystyrene with molecular weight ranging from 162 to 30,230 Da. The elemental composition of the solid was determined using Elemental Analyzer (Interscience Flash 2000). The chemical nature of the solid investigated by means of Fourier Transform Infrared Spectrophotometer (FT-IR Bruker Tensor 27). pH and TAN were measured using an autotitrator (785 DMP Titrino, Metrohm). The water content of the liquid was determined by Karl Fisher titrations (titrant: Hydranal composite 5, Metrohm 787 KFTitrino). Higher heating value (HHV) was measured using a Bomb calorimeter (IKA C2000 basic).

2.3. Product definition and calculation

Gas, liquid and solid yields were calculated as Carbon-fraction of the wood intake (Eqs. (1)–(3); excluding guaiacol) rather than more common weight fraction to avoid counting the oxygen content or water as valuable product for subsequent conversion to biofuel.

Gas yield was calculated using composition analyzed by the off-line GC, available gas volume and, end pressure and temperature after cooling, using the ideal gas law and defining the available gas volume as being the total volume of the reactor minus the volume of the liquid product. The solid yield was determined based on the weight fraction of solid residue and its carbon content. The liquid yield was obtained by difference for convenience:

$$\mathrm{Yield_{Solid}}\ (\mathrm{C\%}) = \frac{M_{\text{Acetone insoluble}}}{M_{\text{Wood intake (dry)}}} \times 100 \tag{1}$$

$$\mathrm{Yield_{Gas}}\ (\mathrm{C\%}) = \frac{M_{\text{Gas formed}}}{M_{\text{Wood intake (dry)}}} \times 100 \tag{2}$$

$$\mathrm{Yield_{Liquid}}\ (\mathrm{C\%}) = 100 - \mathrm{Yield_{Solid}}\ (\mathrm{C\%}) - \mathrm{Yield_{Gas}}\ (\mathrm{C\%}) \tag{3}$$

where M stands for total mass of the carbon present. It should be noted that by doing so all the losses are attributed to the liquid and hence the liquid yield may be over-reported. However, the validity of the definition of liquid yield (Eq. (3)) was checked and confirmed in the earlier work [7].

The liquid product was further divided into two fractions, based on apparent molecular weight (as determined by GPC), namely