

Liquefaction of Furniture Residues and Pigs' Manure Sludge

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Abstract

The present work reports liquefaction studies of a sludge from pigs production and of a residue produced in a furniture factory. Tests were carried out in a 100 ml reactor with magnetic agitation heated by an oil bath. The effect of the temperature, biomass pre-treatment, type of solvent, type and concentration of catalyst and concentration of biomass was studied. Afterwards, experiments were also performed in a 1L reactor with mechanical stirring and temperature control by a heating mantle. The results obtained in the 100 mL reactor show that it is possible to liquefy 40-65% of the furniture residues using 20% biomass, catalyst A (3-4%), solvent 1 and s (1:1) as solvent at 160°C for 1-2 hours. Biomass pre-treatment with the solvent mixture allows to increase by 15% the conversion after 2h of reaction. Due to more efficient conditions of temperature control and stirring in the 1L reactor higher conversion values are reached. For the manure sludge, it was possible to obtain a liquefaction conversion of the pre-treated sludge of about 70% in only 30 minutes. The use of bio-oil as liquefaction solvent leads to a decrease of the liquefaction yield higher than 20% but it is still a very interesting alternative for costs reductions. The bio-oils were characterized by infrared spectroscopy (FT-mir) and the density, water content and the hydroxyl and acid values were also analysed.

Keywords: liquefaction, furniture residues, pigs' manure sludges.

1. Introduction

Direct liquefaction involves the direct conversion of biomass into a liquid fuel without the production of a gaseous phase. The liquefaction can be held in different operating conditions: high temperatures (>200°C) with pressure (hydrothermal upgrading – HTU)) or in a solvolysis process at moderated temperatures (100-250°C) and atmospheric pressure (Pan, 2011; Braz, 2015). This work is focused on the liquefaction by solvolysis of industrial residues like a furniture residue and the sludges from a pig production waste water treatment plant.

The use of industrial residues as raw-material to liquefaction processes is economically and environmentally very interesting and is a promising alternative to sludge incineration or landfill disposal.

The chemical reactions involved in the liquefaction process lead to the breakdown of the biomass polymers, like cellulose, hemicellulose and lignin. The conversion of the biomass into bio-oil is affected by several variables such as: the chemical composition and concentration of biomass, the type of solvent, concentration and type of catalyst, temperature and reaction time.

Recently much attention has been given to liquefaction of bioresources using polyhydric alcohols due to its high yields and low-cost equipment and reagents, resulting in relatively cheap products. This type of liquefaction is often conducted at temperatures in the range of 150-180°C, at atmospheric pressure and usually with the presence of a catalyst. The liquefaction can be either acid- or base-

catalysed with the former being more common since the base-catalysed liquefactions need higher temperatures (250 °C) to achieve liquefaction yields compared to the obtained by acid-catalysed (Zhang, 2011).

The liquefaction of lignocellulosic materials in polyhydric alcohols combines the reactions of solvolysis, depolymerisation, thermal degradation and hydrolysis (Zhang, 2011; Ballat, 2008) through the following steps: solvolysis resulting in micellar-like substructures; depolymerization to smaller and soluble molecules; thermal decomposition leading to new molecular rearrangements through dehydration, decarboxylation, C - O and C - C bond ruptures and hydrolysis of glycosidic bonds;

This study aims to compare the effects of different operating conditions on liquefaction of swine manure sludge and furniture residue.

2. Experimental Methods

2.1. Materials

Furniture residues, supplied by IKEA, and a pig's manure sludge, supplied by Secil, were used as biomasses. solvent 1, solvent 2 provided by Resiquímica were used as solvents. Catalyst A, catalyst B and catalyst C, and catalyst D. The washing solvents for filtration were acetone (99,6%) from Labchem and methanol (99,8%) from Panreac.

2.2. Liquefaction reaction

The liquefaction reactions were carried out in a three neck reactor of 100 mL with a magnetic agitator. In standard experiments, 5 g of biomass, 25 g of solvent and 0.9 g of catalyst were added to the reactor. The reactor was immersed in an oil bath which was pre-heated up to 10°C above the reaction temperature. One of the necks was attached to a Dean-Stark separator/condenser and a thermopar (with an on-off control) was placed in another neck. The zero time ($t=0$) was considered the time when the mixture reaches the intended temperature. After the reaction, the flask was immersed into ice to quench the reaction. When the temperature reached 80°C, the liquid fraction was separated from the residues by filtration. The residues were washed with acetone and methanol, dried in an oven at 120°C to constant weight and weighed. The conversion defined in terms of mass changes:

$$\%C = \frac{(m_i - m_f)}{m_i} \times 100 \quad (1)$$

Where m_i and m_f are the initial and final mass of the solid fraction, respectively. This equation does not take into account the initial moisture and inorganic residue contents of biomass.

The biomass percentage was determined by the following equation:

$$\%biomass = \frac{m_{biomass}}{m_{solvents}} \times 100 \quad (2)$$

2.3. Characterization of liquefied product

To characterize the liquids obtained by the liquefaction reactions several techniques were applied. The water content was determined by Karl Fischer method with a 831 KF Coulometer, Methrohm. Density was determined with a Densito 30XP from Mettler Toledo, PortableLab. Hydroxyl and acid value were estimated by titration. Mid infrared spectrum were also collected using a FT-MIR spectrometer from BOMEM FTLA2000-100, ABB CANADA equipped with a SiC light source and a DTGS detector.

3. Results and Discussion

3.1. Characterization of the biomasses

Table 1 presents the composition of the two biomasses used in this work.

Table 1 - Biomasses composition.

Biomass	Moisture (%)	Organic matter (%)	Ash (%)
Furniture Residue	6	93	1
Pigs' Sludge	79	11	10

The study of the influence of the several operating variables on the liquefaction yield was carried out in the 100 mL reactor and the results are presented below.

3.2. Effect of the type of biomass and catalyst

3.2.1. Effect of the type of biomass

Figure 1 presents the yield of the liquefaction of the two biomasses obtained in a standard liquefaction experiment.

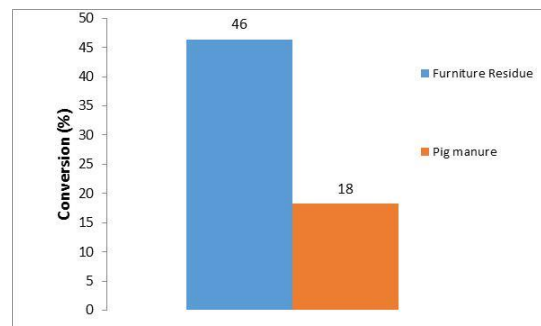


Figure 1 - Liquefaction of furniture residue and pig manure. Conditions: reactor: 100 mL; Biomass-20%, 160 °C, $t=2$ h, p-catalyst A-3%, Solvent 1:Solvent 2 =1:2.

As shown, the furniture residue presented the highest conversion. It is worth mentioning that the high water content of the pig manure did not allow to conduct the liquefaction in the 100 mL reactor. In fact, to be able to reach the desired temperature (160°) it was necessary to use the dried sludge that led to a very low conversion.

3.2.2. Effect of the catalyst

The catalysts tested in this work were: catalyst A, catalyst B and catalyst C.

The results showed that the catalysts that provide the higher conversions were catalyst A and catalyst C. In fact, using 20% of biomass, Solvent 1:Solvent 2 =1:2; 160°C; catalyst -3% and 2h of reaction the conversion was 47% using catalyst A, 44% with catalyst C and only 23% with catalyst B. Therefore, catalyst A was used in the subsequent liquefaction experiments.

3.3. Effect of several liquefaction variables

3.3.1. Biomass concentration

In a liquefaction reaction, the increase of the solid/liquid ratio, which is economically very interesting, is expected to decrease the yield of bio-oil production and increase its viscosity. Therefore, it is very important to optimize this variable. Figure 2 shows that, as expected, the conversion significantly decreases with biomass concentration and so the value of 20% was used in the following experiments.

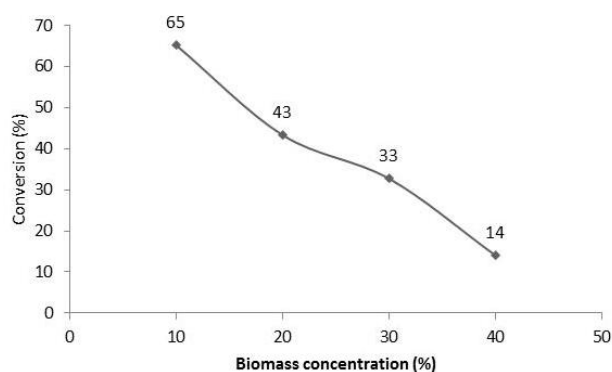


Figure 2- Effect of biomass concentration on the liquefaction conversion. Conditions: furniture residue; reactor: 100 mL; 160 °C, 1h, catalyst A-3%, Solvent 1:Solvent 2 =1:2.

3.3.2. Solvent composition

The yield of the reaction and the properties of the bio-oil are strongly affected by solvent composition. In this work, liquefaction experiments were carried out with Solvent 1: Solvent 2 (1:1); Solvent 1: Solvent 2 (1:2) and Solvent 2. The use of bio-oil as solvent was studied in the liquefaction experiments in the 1L reactor.

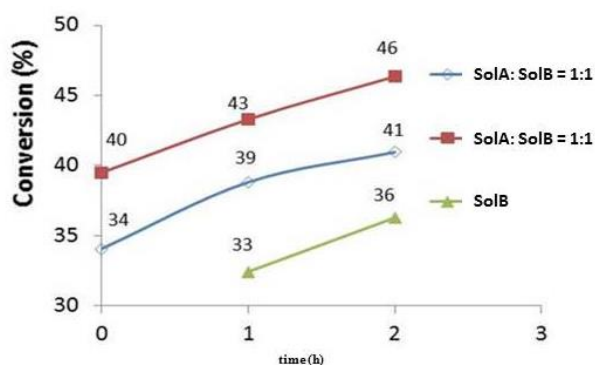


Figure 3 – Effect of solvent composition on the liquefaction of the furniture residues. Conditions: reactor: 100 mL; 20% biomass; 160 °C, 1h, catalyst A-3%, Solvent 1:Solvent 2=1:2.

As shown above, the solvent that led to the best results was Solvent 1: Solvent 2 (1:1). Using higher amounts of Solvent 2 was unfavourable to the reaction but decreased the viscosity of the bio-oil. The density of bio-oil was slightly affected by the type of solvent: 0.99 kg/dm³ for Solvent 1:Solvent 2 (1:1), 0.94 kg/dm³ for Solvent 1:Solvent 2 (1:2) and 0.86 when using only Solvent 2.

Figure 3 also illustrates the effect of the reaction time on the liquefaction yield. It is worth noting that the reaction occurs during the heating time t , leading to a significant conversion at the zero time. Afterwards, the increase of the conversion is slow and around 3-5% per hour.

3.3.3. Temperature

As presented in Figure 4, the conversion increases with the increase of the temperature. Thus, at 180°C and 160°C, 50% or 40% of the biomass is converted during the heating time which was ≈ 15 min at 180°C and 9 min at 160°C. After reaching the desired temperature, the augment of the yield in 2h is 13 % at 180°C and only 6% at 160°C.

Some authors state that if the temperature is too high it may lead to repolymerization and condensation reactions, increasing the amount of residues (Celikbag *et al*, 2014). In this study, at 180°C this effect was not yet observed.

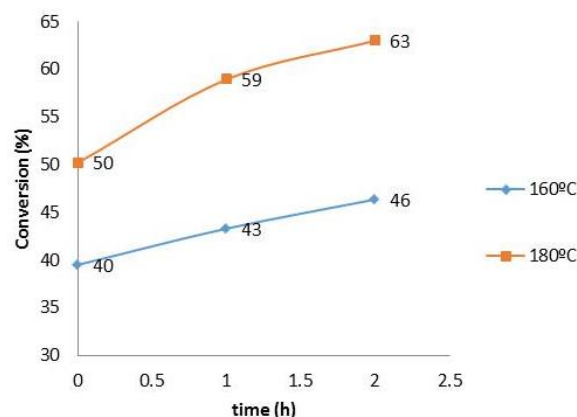


Figure 4 - Effect of the temperature and time on liquefaction conversion. Conditions: reactor: 100 mL; 20% biomass; catalyst A -3%, Solvent 1: Solvent 2 =1:2.

3.3.4. Catalyst concentration

Figure 5 shows that the increase of the catalyst amount has a positive impact on the final conversion. However, a higher amount of catalyst also increases the reaction costs.

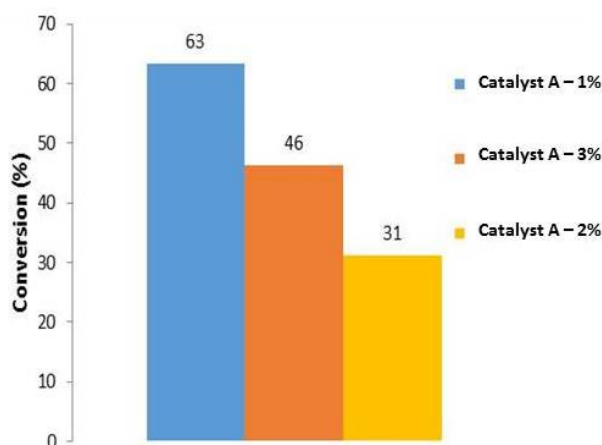


Figure 5 – Effect of the catalyst on the liquefaction of the furniture residues. Conditions: reactor: 100 mL; 20% biomass; 160 °C, 2h, Solvent 1: Solvent 2=1:1

Comparing Figure 4 and 5 it is possible to conclude that the increase of the temperature from 160°C to 180°C had the same effect as the increase of the catalyst concentration from 3 % to 4%.

3.3.5. Pre-treatment

The pre-treatment was carried out by spraying the biomass with the solvent the day before the experiment so that the biomass could absorb it, promoting the swelling of the cells and increasing the accessibility of the catalyst.

As shown below, the pre-treatment of this biomass with the solvents allowed increasing $\approx 7\%$ its conversion in bio-oil. In fact, after 1h of reaction it was possible to convert 50% of the pre-treated residue in only 1h, whereas this value was only 43% for the as-received biomass.

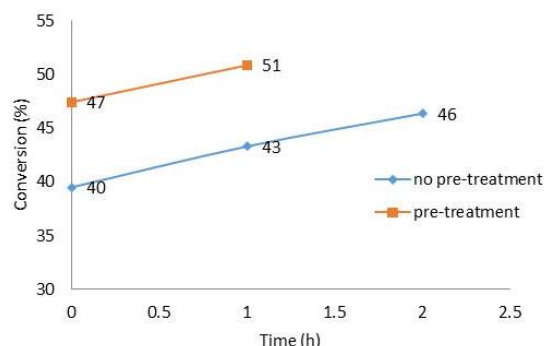


Figure 6 – Effect of the pre-treatment on the liquefaction of the furniture residues. Conditions: reactor: 100 mL; 20% biomass; 160 °C, Solvent 1: Solvent 2=1:1; catalyst A-3%.

3.3.6. Scale-up experiments

To evaluate if the reactor scale-up affects the liquefaction results, several experiments were carried out in 0.5 L and 1L reactors. As seen in Figure 6, due to more efficient conditions of temperature and agitation control in the larger reactors higher conversion values are reached in only 30 minutes.

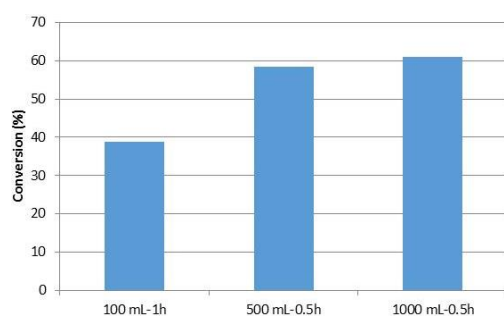


Figure 7 – Effect of the reactor volume on the liquefaction conversion. Conditions: 20% biomass; Solvent 1:Solvent 2; catalyst A-3%; 160°C; 500 rpm.

The effect of increasing the stirring speed in the large volume reactor was also studied. The conversion of the furniture residue into bio-oil was 63% at 100 min⁻¹, 67% at 500 min⁻¹ and 61% at 1000 min⁻¹ (20% biomass, Solvent 1:Solvent 2=1:2, catalyst A- 3%, T=155°C, 0.5h). At 1000 min⁻¹ the turbulence was so high that the reaction pulp was projected to the reactor wall thus decreasing the conversion.

For the manure sludge, it was possible to obtain a liquefaction conversion of pre-treated sludge of about 75% in only 30 minutes, whereas with the as-received sludge the yield was 60%. Accordingly, it is possible to conclude that as observed in Figure 7 for the furniture residue, the pre-treatment with the solvents favored the liquefaction process of pig's manure.

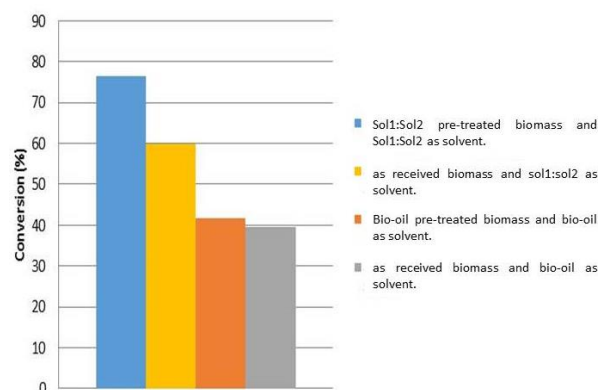


Figure 8 – Effect of the pre-treatment on the liquefaction of as received pig' manure sludge. Conditions: reactor: 1 L; 20% biomass; 155 °C, Solvent 1: Solvent 2 =1:2; catalyst A - 3%; 0.5h.

It is worth mentioning that this as-received sludge contains 79% of moisture, which is an important drawback for the alternative processing technologies.

Figure 8 also shows that the use of bio-oil as the liquefaction solvent leads to the reduction of the conversion of $\approx 20\%$. Even though this alternative is very interesting for costs reductions and the efficiency of the liquefaction can be improved by increasing the contact time and/or by the feed of fresh bio-oil.

The effect of the biomass concentration on the liquefaction reaction in the larger reactor was also studied for the two biomasses (Figure 9).

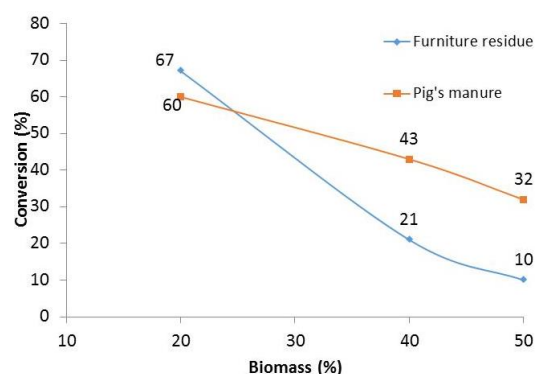


Figure 9 – Effect of the biomass concentration on liquefaction. Conditions: reactor: 1 L; 20% biomass; 155 °C, Solvent 1: Solvent 2=1:2; catalyst A-3%; 0.5h.

Comparing Figure 2 with the results presented in Figure 9 for the furniture residue it is also possible to conclude that the 1L reactor is more efficient than the smaller one. Furthermore, the above Figure shows that the liquefaction

of the pig's manure is not so negatively affected by the increase of the biomass concentration as the furniture residue. Thus, a high initial moisture content of the biomass may allow the use of a larger biomass to solvent ratio, which is obviously more interesting.

3.4. Characterization of biomasses and bio-oils

3.4.1. FT-mir

Figure 10 presents the spectrums of the as received biomasses. The most significant differences are due to high water content ($\approx 79\%$) of the pig's manure. In fact, the peaks at $3200\text{--}3500\text{ cm}^{-1}$ correspond to the stretching vibration of the hydroxyl groups (Zou, et al., 2009) and at 1600 cm^{-1} of the bending vibrations of the OH groups.

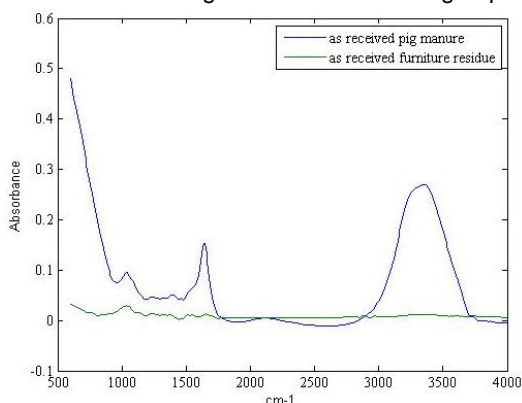


Figure 10– Spectrums of as received and pre-treated furniture residue.

Figure 11 shows the spectrums of several bio-oils produced using the furniture residue and the pig's manure as biomasses. In this case the main peaks are at:

$\sim 3200\text{--}3500\text{ cm}^{-1}$ due to the stretching vibration of hydroxyl groups (Zou, et al., 2009) of the solvents molecules. As expected, this peak is stronger in the bio-oil produced with the solvent mixture with a higher amount of solvent A;

$\sim 2800\text{--}3000\text{ cm}^{-1}$ that corresponds to the C-H stretching (Grilc et al., 2015; Bui et al., 2015);

$\sim 1000\text{--}1600\text{ cm}^{-1}$ that may correspond to several important absorption bands such as: at $850\text{--}950\text{ cm}^{-1}$ related to C-H stretching, $1000\text{--}1200\text{ cm}^{-1}$ due to C-O stretching of the cellulose, $1400\text{--}1500\text{ cm}^{-1}$ associated with C-O stretching in O-CH_3 , $1510\text{--}1600\text{ cm}^{-1}$ related to the lignin's aromatic rings, 1632 cm^{-1} associated with the C=C vibration, 1719 cm^{-1} associated with carbonyl C=O stretching [Zou, et al., 2009; Chen & Lu, 2009; Braz, A. 2015].

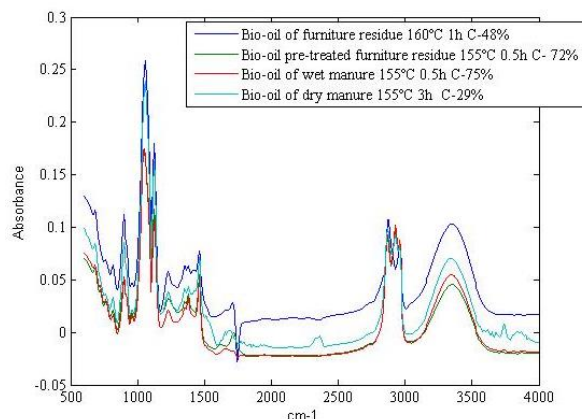


Figure 11 – Spectrums of the bio-oils produced using the two biomasses. Conditions: 20% biomass; catalyst A-3%; as received furniture residue at 160°C : reactor: 100 mL; Solvent 1: Solvent 2 =1:1; pre-treated furniture residue and pig's manure biomasses: reactor: 1 L; Solvent 1: Solvent 2=1:2.

4. Conclusions

The results show that it is possible to liquefy 40-65% of the furniture residues using 20% biomass, catalyst A (3-4%), Solvent 1 and Solvent 2 (1:1), 160°C and 1-2 hours. The pre-treatment of the biomass with the solvents mixture allows to increase by 15% the conversion after 2h of reaction. In the 1 L reactor it was possible to obtain a liquefaction conversion of pre-treated pig's manure and furniture residue higher than 70% in only 30 minutes at 155°C . The use of bio-oil as liquefaction solvent leads to a conversion reduction higher than 20%. However, this alternative is still a very interesting alternative for costs reductions.

5. References

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