Optimisation and overview of pine liquefaction process

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Abstract

Climate change, depletion of fossil fuels and booming economy of developing countries lead global society to search for new technologies of sustainable fuels and chemical production. There are several methods of changing the energy mix and making the inevitable energy transition process smoother. Biomass as a net-zero emission feedstock may be used to foster a change in energy systems by producing energy, fuels and biocomponents e.g. bioethanol. Nevertheless, an optimisation of the process is needed. Herein, a non-pressurised and acid-catalysed liquefaction was investigated. The usage of 2-ethylhexanol as a solvent and p-toluenesulfonic acid as a catalyst for lignocellulosic biomass (i.e. pinewood) transformation via acid liquefaction was studied. Additionally, the trial of the method to remove alkylphenolic fraction from residues created after bioliquefaction using trimethylamine, acetic anhydride and diethyloaminopyridin was examined. During the process, high ratio of biomass-to-solvent (1:1) was achieved. Fourier Transform Infrared Spectroscopy confirmed the presence of alkoxy group, aromatic groups and organic acids in the obtained solution.

Keywords: Biomass liquefaction, lignocellulosis**,** alkylphenolic fraction, deacitilation, acid-catalysed

1. Introduction

The increasing population and technological development have made the world to seek new sources of energy. Nevertheless, fossil fuels, has been a base of the industrial revolution and the boost of economies in the 20th century, still get the major part of the energy mix in future energy scenarios for foreseeable future.
Data from International Energy Agency, year 2019, show significant decrease of oil usage along with augmenting of renewables and natural gas share. OECD countries as well as non-OECD countries in Europe and Eurasia lost their shares of energy supply in behalf of, mainly, non-OECD Asia. Coal, natural gas and oil have been the predominant energy sources. What is more, primary energy consumption increases year by year. Researchers and activists prepared a lot of scenarios showing the possible paths for the global economy fuels usage. World Energy Council proposed three of them called Modern Jazz (market-led, digitally-disrupted world with faster-paced and more uneven economic growth), Unfinished Symphony (a strong, coordinated, policy-led world, with long-term planning and united global action to address connected challenges including inequitable access and affordable decarbonisation) and Hard Rock (a fragmented world with inward-looking policies, lower growth and less global cooperation) [1,2]. Thanks to dotation and support programmes, costs of carbon-free renewable energy technologies such as photovoltaics or wind power plants decreased, their intermittency of energy production creates the need to use a stable resource for electricity and fuels generation – biomass [3].

1.1. Classification of biofuels

According to EU legislation [4] biomass is defined as "*the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste*". First-generation biofuels are generated from edible sources and include mainly ethanol and biodiesel, which are generally produced from the fermentation of C_6 sugars (like glucose) using classical or GMO yeast strains [5]. Second-generation biofuels are produced from non-food crops including waste from food crops, agricultural residues, wood chips and waste cooking oil. This kind of feedstock is the non-edible by-product of food crops [6]. The main component of *third-generation biofuels* are microalgae and microbes. It is currently considered to be a feasible alternative renewable energy resource for biofuel production that could overcome the disadvantages of first and second-generation biofuels. Microalgae can provide several different types of biofuels. This includes methane, biodiesel and bio-hydrogen [7]. *Fourth-generation* uses genetically modified algae to enhance biofuel production [8]. World Energy Council divides biofuels into two types, which are bioethanol and biodiesel. IEA defines biofuels as 'liquid and gaseous fuels produced from biomass'. However, there are some solid biofuels as well [9].

1.2. Types and sources of biomass

According to European Commission, biomass is '*biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste*.' [10]. It can be categorised into several types, by energy crop, by-products, end use materials and biomass origin i.e. woody biomass, herbaceous biomass, municipal waste etc. [11,12,13].

1.3. Resources and composition of lignocellulosic biomass

Lignocellulosic biomass such as rice straw, switchgrass etc. are considered as important renewable feedstock, which could be utilized to produce biofuels like bioethanol, biogas etc. Composition of lignocellulose biomass is primarily composed of plant cell wall containing carbohydrates, cellulose, hemicellulose, lignin and heterogeneous phenolic polymers as structural components [14]. Cellulose is the most abundant biopolymer available in nature, because it is one of the major components of the cell walls of majority of the plants. Cellulose is the reason of a strengths of plant's cell walls. Moreover, it makes the lignocellulosic matrix very resistant to enzymatic hydrolysis. It owes its structural properties to the fact that it can retain a semi-crystalline state of aggregation even in an aqueous conditions. Thanks to changes in DP (degree of polymerization), which is the number of glucose units in the polymer, we may alter the lignocellulosic biomass' recalcitrance, by causing changes in crystallinity and porosity, however, the exact role is still not clear and needs to be investigated individually [15]. Hemicelluloses are heterogeneous group of biopolymers, polysaccharides in plant cell walls. The DP of it is in the range of 100-200 units, which is much lower in comparison to cellulose. All types of hemicelluloses can be found in the cell walls of all terrestrial plants. The detailed structure of the hemicelluloses and their availability vary widely between different species and cell types. The most important biological role of hemicelluloses is to strengthen the cell wall by interaction with cellulose and with lignin, in

some cases. Hemicellulose may play this role thanks to its branched structure [16,17]. Lignin, making up to 10–30% of lignocellulosic biomass, is the second most abundant natural polymer. Lignin is a very complex, amorphous heteropolymer, insoluble in water and stable in nature, acting as a gluing substance between cellulose and hemicellulose. Lignin is a three-dimensional, highly cross-linked macromolecule composed of three types of phenols, which include: coniferyl, sinapyl, and p-coumaryl alcohols, yielding a vast number of functional groups and links. It plays a negative role in the conversion of cellulose, it may physically limit polysaccharide accessibility, blocking the access of the enzymes to cellulose. Therefore, removal of lignin increases the porosity [17,18]. Other components consist of acetyl groups, ash content and other individual compounds. Acetyl groups in lignocellulosic biomass affect properties and interactions with other polymers, affecting their possibility of being extracted and solubility. Nevertheless, details of those interactions are still largely obscure [19]. Five most abundant elements in biomass, being a part of ash, which contains mineral content are: silicon, potassium, calcium, sulphur and chlorine, silica having the biggest content. In case of lignocellulosic biomass' incineration in boilers, it has to be removed and disposed, because of the possible slag formation opportunity, which enhances costs [20]. Because of diversity of extractives, no generalized procedures for isolation and determination of individual compounds is established. The most important ones are: volatile materials (terpenoids and terpenes), non-volatile extractives (e.g. resin acids), phenolic extractives (tannins and flavonoids) and soluble carbohydrates and other polar extractives (e.g. pectines) [21].

1.4. Pre-treatment processes

The presence of lignin and hemicelluloses hinders the efficiency of biomass conversion to useful fuels and materials, because of its barrier functionality. Therefore, pre-treatment is often needed to change the physical and chemical properties of lignocellulosic biomass in order to facilitate the conversion processes. Those processes can be classified in one of five categories. Chemical processes, such as organic solvents usage, ionic liquids method or wet oxidation improve biodegradability of cellulose due to lignin and/or hemicellulose removal. Their advantages are, besides aforementioned process, increasing accessible surface area. Nevertheless, they are, on the whole, corrosive, expensive and some of them require long residence time [21,22,23]. Mechanical/physical processes, such as grinding or milling, convert biomass particles into smaller pieces. Thanks to such treatment, accessible surface area is increased, crystallinity and cellulose's degree of polymerization are decreased. Nevertheless, they are energy inefficient [21,24,25]. Physico-chemical methods, exemplary steam or CO_2 explosion, reduce crystallinity of cellulose as well and, what is more, improve the accessibility of it to the hydrolytic enzymes. Nevertheless, as mechanical processes, they are energy inefficient and expensive [20,21,22]. Thermochemical process, such as torrefaction, rely on heat and chemical catalyst impact to synthesize useful energy. They are highly efficient, versatile and are useful for wide range of feedstocks. On the other hand, they is also a possibility of producing reactive ashes in this process [25,26]. Lastly, biological processes, which are mostly associated with fungi action, that are capable of producing enzymes useful in lignin or hemicellulose degradation. They can be conducted in low temperatures and consume small amount of energy. However, the rate of hydrolysis is very low there [21,22,27].

1.5. Conversion of biomass

There are several process of thermochemical conversion of biomass. Some of them are direct combustion, gasification and pyrolysis. The objective of direct combustion process is to produce heat and the electricity, possibly in cogeneration. Combustion processes involve various reactions, which can be classified as devolatilisation and combustions of carbon generated in the process [28]. Gasification is based on conducting pyrolysis or thermal cracking under anoxic conditions to biomass as raw material. [29]. Pyrolysis process, on the other hand is characterised by solid fuel thermal degradation, involving breaking of C-C and C-O bonds through decarbonylation and decarboxylation [30].

1.6. Process used in Master Thesis

Acidic liquefaction, which was examined in this Master Thesis, is a brand new process among all the biomass processing methods. Thanks to usage of polyhydric alcohols such as 2-ethylhexanol along with acid based catalyst such as p-toluenosulphonic acid, this process can be used to produce polyols and adhesives. On the whole bioliqufaction brings several reactions, that occur inside the designed reactor, the main being biomass degradation, esterification and polycondensation. The first one is characterized degradation of macromolecule compounds in biomass into small molecules with or without catalyst in the aqueous medium or using organic solvent [31]. After that, reversible reaction limited by the low equilibrium conversion and slow reaction rate occurs, recently performed with excess alcohol to shift the equilibrium conversion, which is called esterification [32]. Finally, polycondensation, which is simply a stage of residue content rising as a function of time occurs. The formation of residues is due to the condensation between depolymerized cellulose and aromatic derivatives of lignin [33]. Even though, the acidic liquefaction process with usage of polyhydric solvent is not yet fully discovered, some researchers such as Kumar A., Adamopoulos S. or Mateus M.M. struggle to move this issue forward. It was concluded, that usage of acidic catalyst, creating acidic conditions in the reactor, can be favourable to liquefaction processes of the lignin and cellulose at the cost of condensation and that the step determining the wood liquefaction was the depolymerisation of cellulose. This may suggest, that the condensation reaction occurred because of the mutual reaction among depolymerized cellulose and degraded aromatic derivatives from lignin part of the biomass [34]. In case of amorphous structures of lignin and hemicellulose, in acidic-catalysed liquefaction temperatures such as 150 °C, structures break into smaller parts, for instance, into oligosaccharides. Solvent used is of importance in the reaction as well, due to the fact, that it determines the products obtained at the end of the process. As mentioned, the process is quite unstudied yet, but researchers such as prof. Rui Galhano dos Santos or prof. João Bordado examine such processes in their daily work [35]. After extraction, the solutions is being filtered into organic phase and aqueous phase. In early stages of reaction glucosides are formed and afterwards, these glucosides subsequently decompose.

2. Materials and methods

2.1. Feedstock

Chips made from pine biomass from Versele Laga were used as biomass feedstock. Materials was crushed an pre-treated with bio-oil from Secil, cement production company. Solvent used in an experiment was 2-ethylohexanol. P-toluenesulfonic acid was a catalyst in the process.

2.2. Procedure and equations

Bio-liquefaction process parameters were: time (120 [min]), temperature (160 [°C]), pressure (ambient). Moreover, rotary evaporator parameters were: pressure (90 [mbar]) and radial velocity: 100 [rpm]. Biomass moisture was assessed. Afterwards, biomass, solvent and catalyst were inserted into the reactor. The initial composition inside the reactor was: initial ratio of biomass to solvent was 1:5, with 3% of added catalyst, calculated from biomass mass. bio-liquefaction is in process for 120 [min]. After bio-liquefaction finish, reactor needed to cool down. After cooling to room temperature, biomass was moved to the empty container and then filtrated. Solid residues were subjected to the viscosity test. Solid residues were then subjected to trial of alkylphenolic fraction removal and glycosides hydrolysis, where water was added to the residues. The amount of water was equal to 50% of the residues mass obtained from direct liquefaction process. TEA was added then to basify the solution. The amount of TEA depended on pH measurement. The ideal pH was supposed to be between 8 and 9. To check pH level, litmus paper was used. Solution after that was heated in 60 [°C] for 3 [h]. It was then filtrated using paper filter and vacuum pump. Treated residues were moved to rotary evaporator to dry under vacuum conditions for 2 [h] in 60 [°C]. Mixture of acidic anhydride and DMAP was added to the residues coming from rotary evaporator. Solution residues in ambient temperature for at least 12 [h]. After that period of time, solution was be heated in 40 [°C] during 4 [h]. Then the solution was put in the rotary for another 4 [h]. Equations used are presented in the table below:

Table 1: Equations used in Thesis

Measured unit	Equation
Yield of the biomass [%]	$Yield = \dfrac{Mass\ of\ solid\ residue\ at\ the\ end\ of\ the\ experiment}{\sum Biomass\ mass\ from\ additions}\ x\ 100\ [\%]$
Mass used for examination after liquefaction procedure [g]	$m_{total} = m_{biomass,total} + m_{solvent,total} + m_{catalyst,total}$ $- m_{unscraped\ mass\ from\ the\ rector\ walls}$ $- \sum m_{evaporated\ water}\ [g]$
Moisture [g]	$Moisture = 1 - \dfrac{m_{final}}{m_{initial}}\ x\ 100\ [\%]$
Water used for akylphenolic fraction removal [g]	$m_{water} = \dfrac{m_{biomass,final\ from\ direct\ liquefaction}}{2}\ [g]$
Amount of TEA [g]	$n_{PTS} = \dfrac{m_{PTS}}{M_{PTS}}\ [mol] \qquad m_{TEA} = n_{PTS}\ x\ M_{TEA}\ [g]$
Amount of acidic anhydride [g]	$m_{acetic\ anhydride} = 0{,}1\ x\ m_{biomass,used}\ [g]$
Amount of DMAP [g]	$m_{DMAP} = 0{,}05\ x\ m_{biomass,used}\ [g]$
Total mass for alkylphenolic fraction removal treatment [g]	$m_{total} = m_{biomass,used} + m_{acetic\ anhydride} + m_{DMAP}\ [g]$
OH number [-]	$OH\ number = \dfrac{C\ x\ m_{KOH}\ x\ (V_{white\ sample} - V_{sample})}{m_{sample}}$

,where:

$m_{initial}$ – biomass mass before drying, m_{final} – biomass mass after drying, C – is the concentration of the KOH

solution, which is 0,5 [mol/L], m_{KOH} – is the molecular mass of the KOH, which is 56,1 [g/mol], $V_{white\ sample}$ – white sample volume [ml], V_{sample} – examined sample volume [ml], m_{sample} – examined sample mass [g]

2.3. Product analysis

Product analysis consisted of OH number (hydroxyl value) measurement and Fourier Transform Infrared Spectroscopy. The hydroxyl value of a substance is the amount, in milligrams, of potassium hydroxide required to neutralize any acid when combined by acylation in 1 g of the substance under examination [36]. Thanks to Fourier transform infrared (FTIR) spectroscopy, analysis and identification of chemical bonds by using an infrared spectrum that is absorbed by the material was able to be conducted.

3. Results and discussion

Pine moisture content was assessed to be 10,90%. Final mass that went for to be furtherly examined was calculated to be 1158,6 [g]. The viscosity test was performed for final bio-oils and residues. Unfortunately, the test could not be performed within the range of used viscometer at any temperature within the temperature range of the equipment. The only viscosity experiment that gave the results within the range of the equipment was Secil bio-oil viscosity test. The result of this test is for 50 [°C] the viscosity was 0,3 [P]. Below, there are presented results of the tests from alkylphenolic fraction removal trial. As derived from equation (2), the amount of biomass used in further experiment is 1158,6 [g]. Amount of water added to a solution was calculated to be 579,3 [g]. In pH adjustment, the amount of PTS acid used in the experiment needed to be assessed. Therefore:

$$n_{PTS} = \frac{37}{172,2} = 0,21\ [mol] \qquad\qquad m_{TEA} = 0,21\ x\ 101,19 = 21,74\ [g]$$

which was defined as a minimum amount of TEA that should be used to make the pH of the solution suitable for further processing. In the end, in order to get the proper colour on the litmus paper, 23 g of TEA were used to basify the solution. The mass of residues for rotary evaporation was 1000,25 g. Due to the small bubble flask volume, rotary evaporation needed to be conducted three times. Table 2 represents the volume of evaporated liquid at each liquefaction and its total sum. Mass difference represents possible losses of material due to suck effect of the vacuum in rotary evaporator, the need to clean the neck of the bubble flask or human error (for instance, caused by bad insertion of the material to the flask)

Table 2: Rotary evaporation results of direct pine liquefaction residues treated with TEA

	Initial material mass [g]	Evaporated water mass [g]	End material mass [g]	Difference [g]
Sum	959,32	53,81	859,21	46,30

The mass that reached the point of experimentation, named as a "end material mass", was treated with acetic anhydride and DMAP. Therefore, acetic anhydride mass was 85,92 [g] and DMAP mass was 1,72 [g]. Total mass

of the solution was 946,85 [g] Overall mass put inside the rotary evaporator was 912,80 g. Allegedly, the difference of mass came from the fact that there was no possibility to scrap the reactor out of every particle possible. Table 3 represents the volume of evaporated liquid at each liquefaction and its total sum. Mass difference represents possible losses of material due to aforementioned reasons.

Table 3: Statistics from rotary evaporation after alkylphenolic fraction removal

Evaporation number	Initial material mass [g]	Evaporated liquid mass [g]	End material mass [g]	Difference [g]
Sum	887,88	7,69	876,0	11,88

Final sample was in the end retrieved to FTIR test, performed 4 times. The OH number turned out to be 58,19.
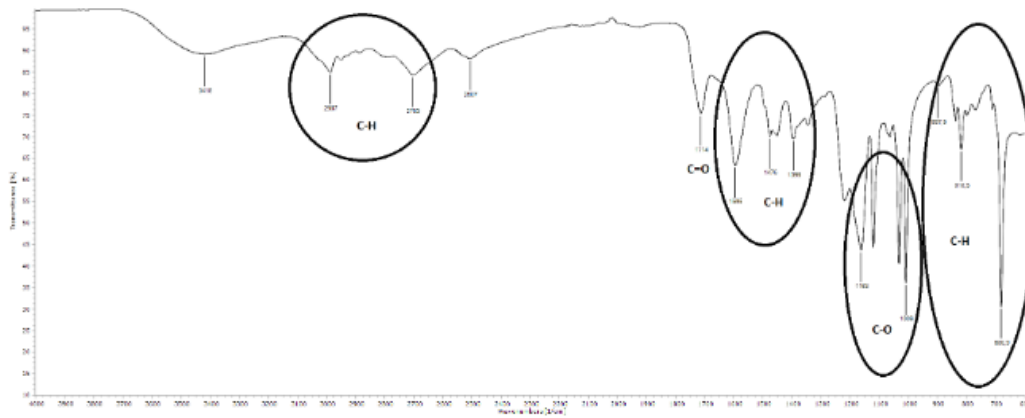

Figure 1: Perkin-Elmer screenshot of liquid sample filtrated after TEA treatment
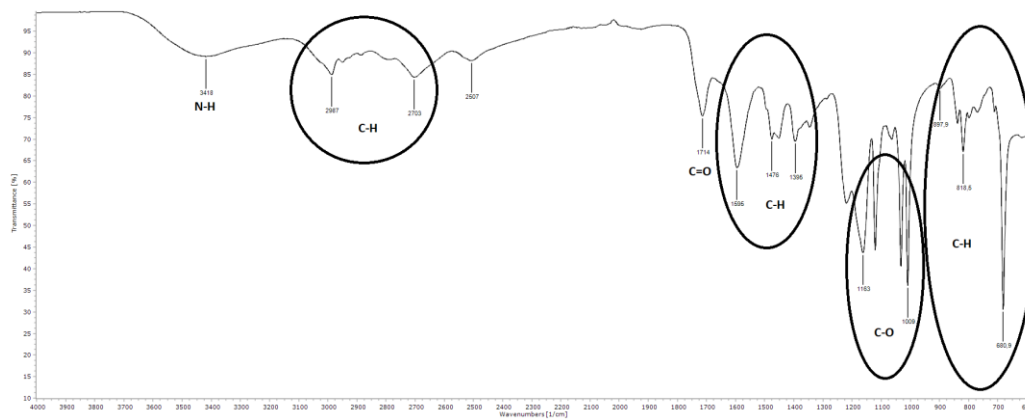

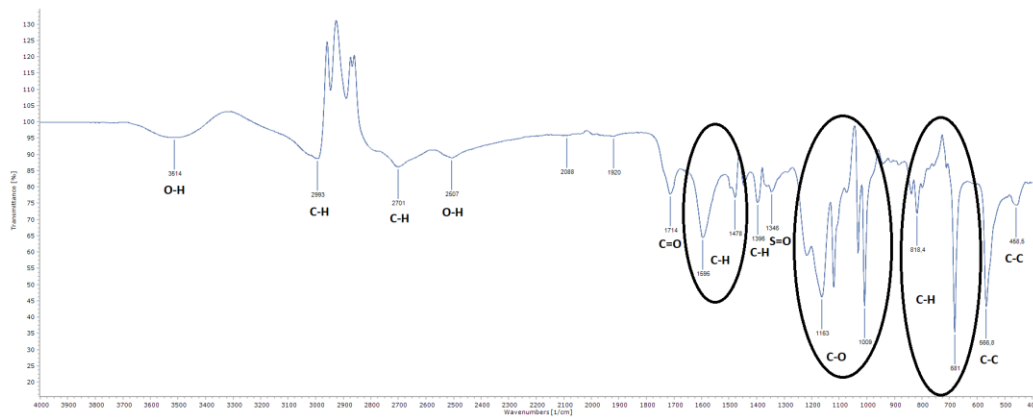*Figure 2: Liquid sample after TEA treatment FTIR with marked bonds.*

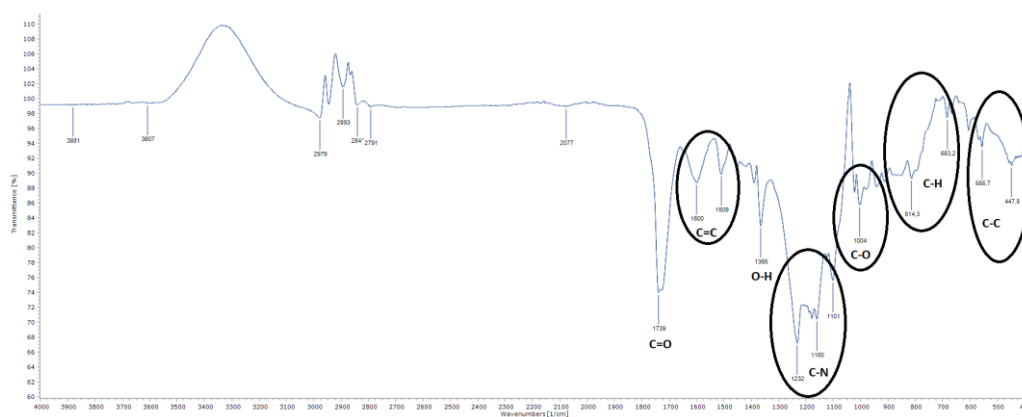*Figure 3: Liquid sample after direct liquefaction FTIR with marked bonds*

Figure 4: Residues after acetic anhydride and DMAP treatment FTIR results

All of the groups, presented in Table 4 were found in the experiment.

Table 4: Functional groups encountered in samples of bio-oils and residues in FTIR analysis

Functional groups	Wavelength	Components
O-H stretching	3700 – 3200	Alcohols, phenols
C-H stretching	3100 – 2800; 1465 – 1365	Alkanes, alkenes
C=O stretching	1760 – 1685	Aldehydes, ketons, carboxylic acids
C=C stretching	1678 - 1575	Alkenes, aromatic compounds
C-H stretching	1465 – 1375	Alkanes, aldehydes
C-O stretching	1300 – 1000	Phenols, esters, primary, secondary and tertiary alcohols
C-H bending	900 - 650	Aromatic compounds

4. Conclusions

To summarise, in this work, liquefaction of the pine wood was conducted in order to check the ability

of the feedstock as a fuel in a direct liquefaction, initially for company Respol Resinas S.A. New method to

increase the number of sugars was involved as well. The liquefaction conditions for pinewood were optimised to reach biomass to solvent ration of 1:1 (m/m). The solvent, that has been used, 2-ethylhexanol, yielded around 55% conversion of initial biomass. To achieve this conversion, ambient pressure, temperature of 160 ^{o}C and process time 2 hours for every biomass addition in laboratory scale is required. Although, this is a promising technique for biomass conversion, as it does not involve any pressured setting and is an inexpensive process that could decrease both fixed and variable costs of the installation. The catalyst used, p-toluenesulfonic acid, needed to be applied in concentration 3% of the initial solvent mass and 3% for every biomass addition, which is 2,6% of concentration overall. Basification using triethyloamine and further experimentation with dimethyloaminopyridine and acetic anhydride led to the creation of a viscous residue that was not able to be examined within the range of viscometer. Used method and the results poses a question whether another method could be used to increase the amount of sugars at the end of the process to satisfactory 60-70% from aqueous phase. Calculation of OH number of final residue sample took place as well. The result obtained lower than usual OH numbers for the bio-oils. The viscosity was also tested. Due to the low range of the equipment having been used, samples of the bio-oil and residues were either under the range of the equipment or over it. At the end, FTIR analysis were conducted. FTIR samples proved the formation of new structures, typical for bio-oils such as aromatic compounds, alkanes. In the sample the materials having been used, such as DMAP or PTS acid were also detected at the specific ranges of the wavelength. In conclusion, the method used for bioliquefaction purposes can be used for further examination in bigger, industrial scale, creating chance of new and sustainable fuel and chemicals creation.

4. Future work and recommendations

Direct liquefaction in ambient pressure is an extremely promising process and needs to be further studied and optimised. Pine liquefaction in Portugal has a chance to become promising technology of fuels production to be used instead of fossil fuels and sustainable chemicals. This subject needs to be studied more in order to develop, for instance, ways to recover the unreacted solvents from bio-oil for re-use.

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