PYROLYSIS OF LIGNIN-RICH BIOMASS FOR RENEWABLE AROMATICS

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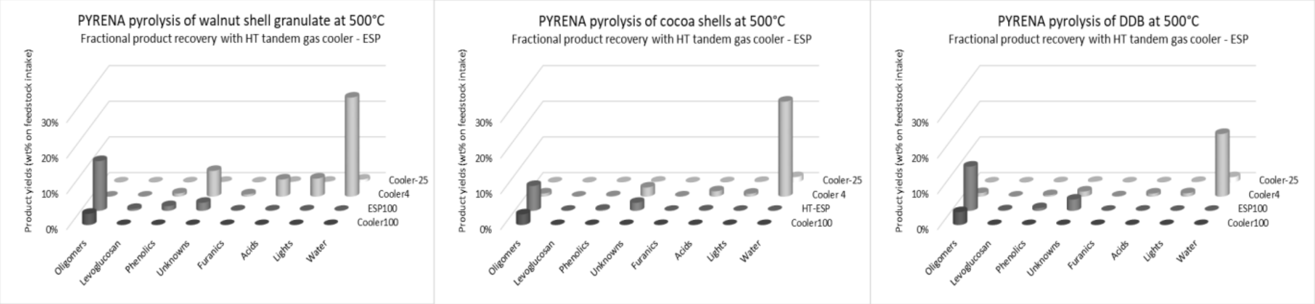
Key Words: Biorizon, Biomass residues, Pyrolysis, Product separation, Applications.

Currently, several national projects are conducted as an activity along the thermochemical horizon towards functionalized aromatics from lignin and lignin-rich biomass sources in the framework of the BIORIZON shared research center in the south of the Netherlands [1]. Regarding the pyrolytic valorization of lignin-rich biomass towards aromatic chemicals for various applications, it is thought that the collection of pyrolysis vapors in separate fractions [2] offers interesting opportunities for valorization, e.g. towards (additives for) bitumen, resins, rubber and specific marine biofuels. For these high market volume – medium market value products, earlier work has revealed that the application of lignin as such (so without derivatization / modification) was not successful because of various incompatibilities. Consequently, it was deduced that specific depolymerized fractions from lignin-rich residues would possibly be usable because of lower molecular weight and/or higher reactivity and/or better miscibility with their petrochemical counterparts.

PYRENA (PYrolysis for RENable Aromatics) features integrated char combustion in a bubbling fluidized bed to generate process heat for pyrolysis in an internal riser reactor [3]. The gaseous pyrolysis products and aerosols are in-situ separated and collected via innovative methods such as high-temperature electrostatic precipitation and low-temperature continuous distillation. The major goal is to achieve a progressive separation between higher molecular weight material such as monomeric and oligomeric phenolics and anhydrosugars, lower molecular weight material such as specific polysaccharide degradation products and water.

DDB (dried distilled biomass, a straw-derived biorefinery residue with ~50 wt% lignin), agro-food walnut shell granulate (~50 wt% lignin) and crushed cocoa shells (~20 wt% lignin and polyphenolics) were pyrolyzed at 500°C to collect specific organic fractions, that might be applicable for bitumen, rubber, resins and marine fuel, products that constitute relatively large markets with medium value.

Pyrolysis of the three feedstocks gave comparable results with an overall mass balance of 85 – 97% (liquid yield ~40-60%), based on the intake of feedstock. The pyrolysis liquids contained approximately 40 – 60% organics (light, medium and heavy molecular weight species). The largest amount of pyrolysis liquid (mainly water and medium to light organics) was collected in the ice-water cooled condenser while most of the heavy and medium molecular weight material (mostly lignin-derived oligomeric products) ended up in the high temperature gas cooler and ESP. Regarding the monomer composition of the different fractions, the major feature is the fact that the ESP mainly traps phenolics, while the ice-water cooled condenser collects the lighter, lower boiling components. See figure below.



The heavy molecular weight material from the 100C cooler and the ESP blends well with commercial shipping fuel and bitumen. The work conducted, indicates that pyrolysis products can be recovered in usable fractions such as monomeric phenols, oligomeric phenols, char and combustible gas. The progress in industrial application trials for bitumen, rubber, resins and marine biofuels with residue-derived pyrolysis oils will be highlighted and an outlook will be provided of potential end-uses for the fractionated pyrolysis products.

For this work the financial support of the Dutch Ministry of Economic Affairs is gratefully acknowledged.

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A SURROGATE MODEL CONSTRUCTION STRATEGY FOR BIO-OIL USING ReaxFF MOLECULAR DYNAMICS

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Key Words: Surrogate model, multi-component bio-oil model, construction strategy, ReaxFF MD, surrogate evaluation

Surrogate fuel model is useful as representative of simplified complex fuel mixture in description of their chemical kinetics in pyrolysis or oxidation conditions. This work propose a surrogate model construction strategy for bio-oil using ReaxFF molecular dynamics. A 24-component bio-oil model was constructed as a baseline model for real bio-oil based on the literature reported data of GC-MS analysis for bio-oil yielded from fast pyrolysis of *Pterocarpus Indicus*. According to the chemical constituent and functional groups in the 24-component bio-oil model, 5 surrogate bio-oil models each containing 6 components were formulated. ReaxFF MD simulations are performed on the 6-component surrogates and the 24-component oil model under the same oxidation conditions. In addition to element ratio comparison, the surrogate models are validated by comparing the simulated temporal evolution of major reactants and products including radicals using the 24-component model as a baseline.

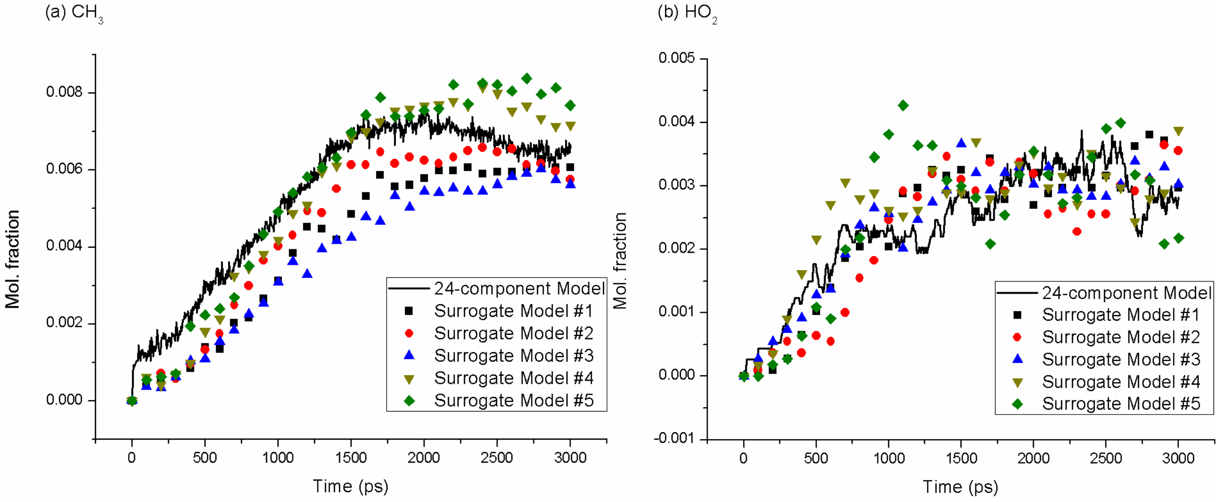

Figure 1 – Time evolution of major small radicals (C_0 – C_2) in different bio-oil oxidation models during the ReaxFF MD isothermal simulations at 1900 K and 5 MPa (a) •CH_3 (b) HO_2•

Analysis shows that all the surrogate models have similar element composition that is very close to the 24-component bio-oil model. By comparing the simulation results, it is shown that model #3 can better reproduce the evolution of fuel and O2; Model #4 has better reproducibility for evolution profiles of CH2O, C2H2O and •CH3; CO evolution is best reproduced by model #2, while H2O by model #5.

This work demonstrates a methodology for investigating the high temperature oxidation pathways of complex fuel systems with ReaxFF MD simulations permitted by the comprehensive reaction analysis capability of VARxMD[1]. It is also a new attempt to have bio-oil surrogate models evaluated with ReaxFF MD simulation, which should be more feasible an approach for validation of surrogate chemical property theoretically[2].

Acknowledgement: This work was supported by National Natural Science Foundation of China under Grant [91641102].

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THE INFLUENCE OF LIPIDS ON THE FATE OF NITROGEN DURING HYDROTHERMAL LIQUEFACTION OF PROTEIN-CONTAINING BIOMASS

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Key words: nitrogen, hydrothermal liquefaction, Maillard reactions, lipids

Nitrogen (N) in the bio-crude obtained from hydrothermal liquefaction (HTL) of protein-containing biomass not only reduces the heating value of fuels, but also increases cost for upgrading to meet the existing fuel standards. Considerable work so far had been focused on N-containing heterocycles formed via Maillard reactions. However, limited information is available on the influence of lipids, as the amides formation could compete with the Maillard reactions, further affecting the fate of N. The objective of this work is therefore to identify the influence of lipids on the nitrogen distribution in the different product phases, with a particular focus on the reaction of N-containing compounds, trying to achieve deeper understanding about reaction mechanism of HTL.

In this study, we tested a set of model compounds (lactose as model carbohydrate, lysine as model protein, palmitic acid as model component of a lipid) to conduct HTL. The model compounds were treated individually and in mixtures at 250 - 350 °C for batch reaction times of 20 min. We investigated the N-distribution in the different HTL-products, mainly focusing on the bio-crude. At 300 °C, only 4.9 wt.% of N distribution (defined as the amount of N in the product relative to that in the feedstocks) is found from HTL of single lysine, while 43.6 wt.% of that is obtained from HTL of the ternary mixture. This is most likely because the higher yield (54.1wt.%) of bio-crude produced from mixture. Specific N-containing compounds in the bio-crude were quantified. With addition of lipids, less yields of typical Maillard reaction products like pyrazines and caprolactam, generated from HTL of carbohydrates and proteins, were obtained, while amides are revealed with significant yield of 2.1 wt.%, indicating that in the presence of lipids, amide formation competes with the generation of Maillard reaction products. These results provide valuable insights for the transformation of nitrogen as well as the reaction pathways of complex systems such as sewage sludge, micro algae, food waste and on the like.

CHALLENGES AND PROGRESS MADE ON THE MICROKINETIC DESCRIPTION OF LIGNIN LIQUEFACTION: APPLICATION OF GROUP CONTRIBUTION METHODS

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Key Words: lignin, pyrolysis, modelling, thermodynamics, group contribution

In this presentation a comprehensive microkinetic modelling framework and experimental tools are used to describe product yield and composition of direct lignin liquefaction processes with and without solvents (See Figure 1). With the framework proposed we aim to develop a unified theory and models capable of describing both dry (pyrolysis) and wet (hydrothermal and solvolysis) lignin liquefaction processes. An important phenomenon that has been shown to occur during lignin pyrolysis (as well as cellulose) is the formation of a liquid intermediate phase, and subsequent ejection of heavy products (>~250 Da) as aerosols from this intermediate. In our presentation we will focus on the nature of lignin pyrolysis liquid intermediate through analysis of phase change equilibria temperatures for relevant lignin fragments, using group contribution methods. Specifically, estimation of boiling (T_b) and melting (T_m) points of lignin fragments was done using ARTIST software (Dortmund Data Bank Software & Separation Technology, GmbH). In total, 50 different lignin fragments were drawn, and their boiling and melting temperatures were calculated. The 50 fragments include monomers, dimers, trimers and tetrameters, with a variety of H, G and S units and inter-unit linkages. Figure 2 shows the calculated phase-change equilibria temperatures plotted against the number of aromatic units in a given lignin fragment. The dotted line at 400 °C is included as the approximate temperature at which both rupture of aliphatic linkages and conversion of short aromatic ring substituents occurs, but is less than the temperature for rearrangement of polycyclic structures. The collection of lignin fragments, such that $T_m < 400 < T_b$, make up the set of molecules that can exist as a liquid intermediate during pyrolysis, and are therefore the ones that have potential to be ejected as aerosols. The average lignin fragment in this range has 2.50 (± 0.11, standard error) aromatic units, molecular weight of 414 (± 20) Da, melting point of 292 (± 13) °C, and boiling point of 573 (± 19) °C. Relying solely on this analysis, one would expect these to be characteristics of an average molecule ejected as a liquid-phase aerosol during pyrolysis of lignin. Based on the quantification of phase equilibria temperatures, this liquid state can contain dimers and trimers, but typically not tetrameters or larger (they will preferentially depolymerize), or monomers (they will vaporize). It is these dimer and trimer products that should make up the majority of the heavy liquid products collected as aerosols. In order to validate this model, comparison was made with previously published work from Pecha, et al. (*Ind. Eng. Chem. Res.*, 56, 2017, 9079-9089) and Bai, et al. (*Fuel,* 128, 2014, 170-179), who analyzed lignin pyrolysis oil with FT-ICR-MS. There is good agreement between the weights of species detected experimentally in these studies and those determined in this work based on group contribution calculations.

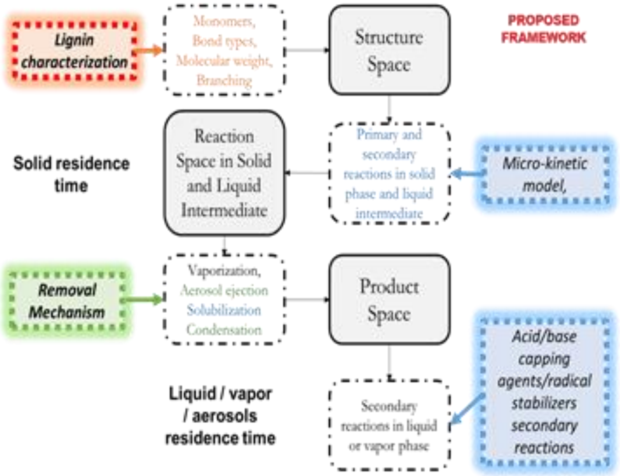

Figure 1. General framework to describe lignin wet and dry thermochemical liquefaction processes.

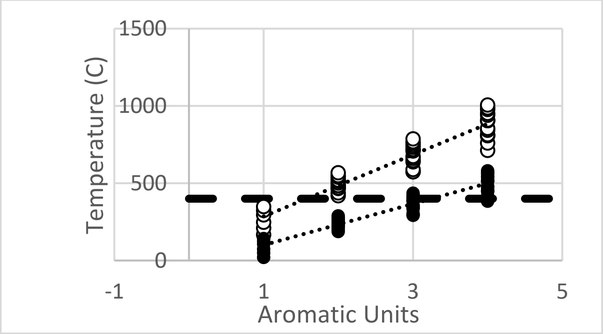

Figure 2. Calculated boiling (open circles) and melting (black circles) temp. of lignin fragments

KINETIC STUDY OF TIRE CARBON BLACK AND BIOMASS SOOT STEAM ACTIVATION USED FOR THE REMOVAL OF PHENOL AND CHLORINE FROM DRINKING WATER

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Keywords: wastewater filters; biomass soot; carbon black from tires; H2O activation; kinetic model.

This study aims to demonstrate a novel method for removing toxic chemicals using soot produced from wood and herbaceous biomass pyrolyzed in a drop tube reactor and tire pyrolytic carbon black. In order to improve the economic performance and reliability of entrained flow gasification, biomass soot has the potential to be captured, activated and further used as a sorbent to remove a broad range of pollutants from wastewater. In recent years, the disposal of waste tires has become an important issue. The liquid hydrocarbons and solid char residue from thermal conversion of waste tires have potential to be used as environmentally benign fuel and activated carbon. In the present work, the influence of ash content, nanostructure, particle size, and porosity on the filter efficiency of steam activated carbon materials was studied. It has been shown for the first time that steam activated soot and carbon black can remove phenol and chloride with the filter efficiencies as high as 95 %. The correlation of the filter efficiency to material properties showed that the presence of alkali and steam activation time were the key parameters affecting filter efficiencies. Kinetic parameters for the steam activation of tire pyrolytic carbon black and biomass soot have been determined by thermogravimetric analysis using steam as an activation agent. The feedstock for the soot production, activation temperatures and residence time were varied. The results showed that the rate of steam activation is 10 times faster than the activation at lower temperature. This study demonstrated that the steam activation process is suitable to prepare activated soot with the high surface area at the short residence time and at temperatures below 800°C. Reaction evolution has successfully been modelled, including the maximum reaction rate obtained in experimental results. Moreover, intrinsic kinetic parameters of the activation reaction order, activation energy and pre-exponential factor – were calculated.

HEAT OF REACTION OF HYDROTHERMAL LIQUEFACTION REACTIONS

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Key Words: Hydrothermal Liquefaction, heat of reaction, blackcurrant pomace.

Wet waste streams include a wide variety of products such as food processing residues, sewage sludge but also the organic fraction of municipal solid waste. Humidity typically varies from 50 to above 90 %. Dewatering and drying is possible for most feedstocks but at a significant cost. Hydrothermal liquefaction produces a biocrude that can be further upgraded into biofuels. The conversion takes place at temperatures between 250 and 400 °C and at pressures above the saturation pressure to ensure that water remains in the liquid phase, typically above 100 bar [1]. Even though the basic principles of hydrothermal liquefaction are well known, there are still some significant scientific questions and technical issues. One of the important questions that remain is the heat of reaction and the heat balance of the reaction.
Hydrothermal liquefaction is performed in the laboratory in batch reactors and in continuous reactors. Industrial applications are only envisaged in continuous reactors. Most scientific work is performed in batch reactors making it difficult to anticipate the results for industrial applications. Typical reactions that occur are de-polymerisation by hydrolysis (100 to 200°C), carbonisation (200 to 250°C), liquefaction (250 to 400 °C) and gasification (350 °C and upwards).

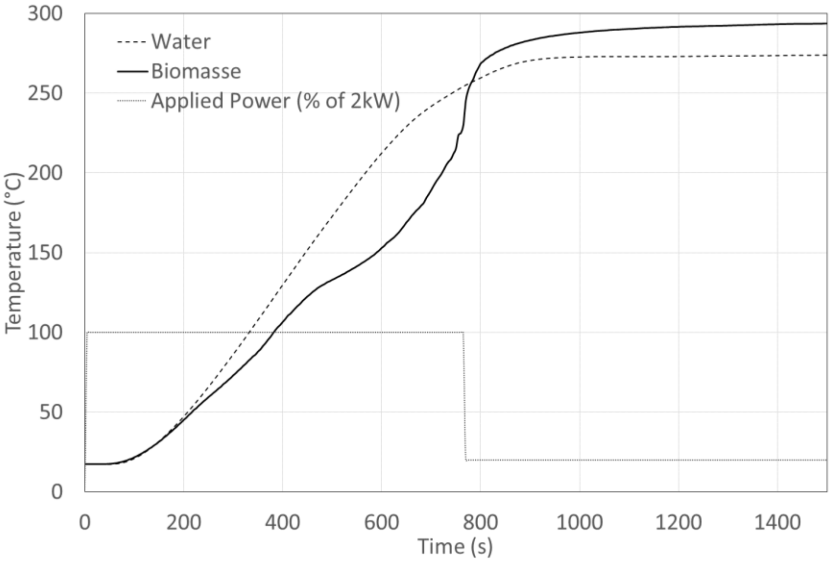

Figure 2 – Temperature response reactor

Figure 1 shows the temperature response of the reactor content with an imposed power. We compare the response of the water biomass mixture with an equal quantity of pure water. The biomass-water mixture is 10% ground blackcurrant pomace in water. The power profile was selected to obtain approximately 300°C with biomass. Precise temperature control is not possible in this case. The difference between the two curved is caused by the reactions taking place in the reactor.

From Figure 1 we can see that the biomass-water mixture heats slower than the pure water content. This is probably due to endothermal de-polymerisation reactions caused by the hydrolysis of the biomass. At about 200°C the biomass water mixture accelerates its heating, compared to the pure water case. During this phase exothermal carbonisation reactions dominate. Above 250°C the hydrothermal carbonisation reactions calm down and liquefaction reactions dominate. In practice the distinction between carbonisation and liquefaction reactions are difficult to make and in reality the frontier is probably not clear cut and difficult to establish.

It is possible to calculate the heat of reaction in the different phases of the experiment. With identical power applied (and assumes identical losses) the biomass case ends up with a higher temperature. This in its own shows that the global reaction is exothermal. The overall heat of reaction is about 0.5 MJ/kg biomass.
This paper presents the results of a study on heat of reaction of the hydrothermal transformation of blackcurrant pomace. The presented results include yield data combined with an energy balance calculated with different techniques.

KINETIC OF BIOBASED BITUMEN SYNTHESIS FROM MICROALGAE BIOMASS BY HYDROTHERMAL LIQUEFACTION

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Key Words: Biomass conversion, Micro-algae, Hydrothermal liquefaction, Bitumen

The current worldwide consumption of bitumen is about 100 million tons. A remarkable combination of properties (adhesion, impermeability to water, specific thermo-rheological behavior) makes it a key material in road construction. Today's bitumen is mostly obtained from petroleum refining, so bioabased alternatives have to be explored for the future. The ALGOROUTE project funded by the French National Agency for Research (ANR) focuses on the use of hydrothermal liquefaction (HTL) process for the production of bitumen mimicking binders from microalgae biomass. HTL applied to microalgae is inspired by the geological process of petroleum formation, but on a very short time scale: For conditions around 260 °C / 50 bar, bitumen like products have been obtained by our consortium for residence times of about 1 hour [1] [2]. Beside temperature and pressure, the key parameters are the reaction time, algae/water ratio and loading level of reactor.

In order to study the kinetics of bitumen formation, an experimental setup allowing fast heating and cooling rates has been developed. It consists of stirred pressure reactor (300mL) combined with an induction heating system and a water/air spray quenching. The cavity or the reactor is instrumented with a pressure sensor and 9 thermocouples for monitoring of the temperature field (Figure 1), with the objective of understanding the physical and chemical phenomena taking place during the process.

Beside, the origin of the bitumen like behavior needs to be clarified. Using biomass from Spirulina microalgae, controlled HTL leads to an hydrophobic product composed of an oil phase and solid residues. The oil phase has a rheological behavior similar to that of a classical bitumen (Figure 2), while the whole hydrophobic product behaves like bitumens formulated with elastomer additives (Figure 2).

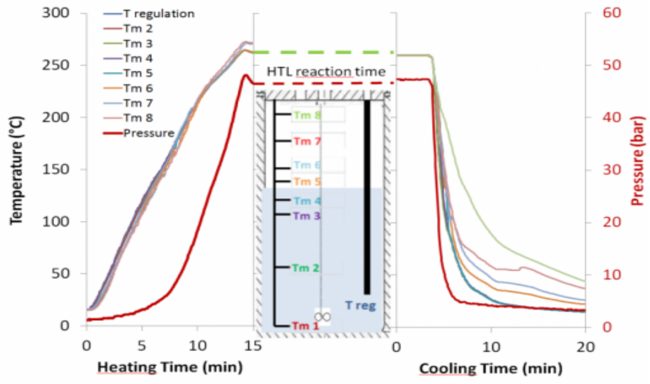

FIGURE 1

Temperature control of the instrumented stirred pressure reactor

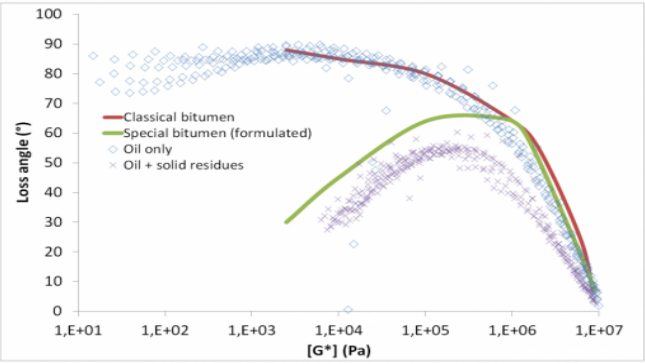

FIGURE 2

Rheological behaviour of oil and oil/solid residues mixture obtaines after 60 min at 260 Celsius degree

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PRODUCTION OF ETHYL ACETATE FROM PYROLYSIS OF LIGNIN MODEL COMPOUND GUAIACYLGLYCEROL-Β-GUAIACYL USING TGA-MS

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Key Words: Pyrolysis, guaiacylglycerol-β-guaiacyl, GGE, ethyl acetate, lignin

Due to the complex chemical structure of lignin, the fundamental chemistry underlying its pyrolysis behaviour is poorly understood. A detailed knowledge of this chemistry would allow for the construction of detailed predictive chemical kinetic models, which could be used to maximise the efficiency of the pyrolysis process.
Lignin is comprised of three monolignols, guaiacyl, p-hydroxyphenyl and syringyl. These are joined together by aryl ether linkages of which β-O-4 is the most common, representing approximately 50% of the linkages found in lignin.[1] In this study, pyrolysis (20ºC/minute heating rate) was carried out on a lignin model compound, guaiacylglycerol-β-guaiacyl ether (GGE). GGE is composed of two guaiacyl subunits connected by a β-O-4 linkage, making it broadly representative of the lignin motif and as such an important lignin model compound. A detailed understanding of the thermal degradation of GGE under pyrolysis conditions will provide valuable information of the role of the β-O-4 linkage in lignin.

GGE is found to lose mass in two stages corresponding with primary and secondary pyrolysis reactions, similar to those occurring in lignin and at similar temperature ranges.[2] More importantly, the appearance of several peaks in the EI mass spectrum of GGE coincide with this primary mass drop. The time scale as to which these peaks occur leads one to conclude that these mass/charge peaks correspond to important intermediaries in the pyrolysis reactions occurring in GGE. These peaks occur at m/z = 43, 61, 70, 77 and 88 corresponding precisely to the EI mass spectrum of ethyl acetate. These observations provide important insights into the pyrolysis behavior of lignin and the confirmation of ethyl acetate being responsible for the appearance of these mass/charge peaks will be vital in the future development of chemical kinetic models describing lignin pyrolysis.

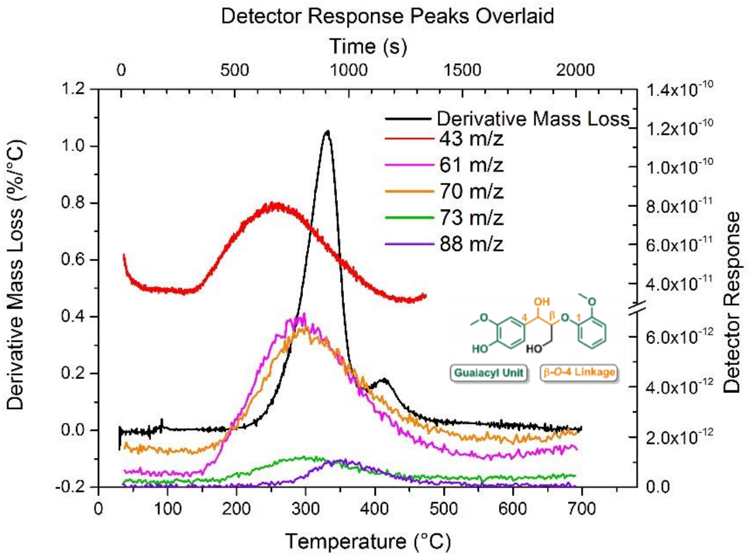

Figure 3. Black line shows the DTG Curve of GGE measured by TGA. Coloured lines show the EI-MS detector responses. The inlet shows structure of GGE

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MANIPULATION OF PRODUCT DISTRIBUTIONS IN BIOMASS FAST PYROLYSIS USING MOLTEN POLYMERS

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Key Words: Biomass fast pyrolysis, Molten polymers, Co-pyrolysis, Selectivity, Pathway inhibition.

Biomass fast pyrolysis has attracted significant attention due to high yields (> 75 wt%) of liquid products. A major drawback to biomass fast pyrolysis is the diverse product distributions of this liquid fraction, making subsequent upgrading and separation operations expensive. Using catalysts to accelerate pathways to desired products have been actively researched to resolve this problem. A complementary strategy is to suppress undesired pathways via inhibition, which is commonly utilized in enzymatic, combustion, and polymerization reactions but rarely explored in biomass fast pyrolysis.
This talk will present the use of molten polymers (MPs) for selective promotion of product yields in biomass fast pyrolysis via the inhibition of undesired pathways. MPs are thermoplastics that melt at high temperatures and have degradation timescales longer than that of biomass. This allows them to be used in biomass fast pyrolysis without decomposition. Using MPs in biomass fast pyrolysis promotes the yields of value-added chemicals via inhibition of physical (i.e., mass transfer) or chemical (i.e., reaction) pathways. It has the potential to reduce the need for subsequent product separation and purification and lead to intensified and inexpensive biomass conversion processes. In our experiments, a custom-made, drop-in, vacuumed batch pyrolysis reactor was employed for the pyrolysis experiments. High-density polyethylene (HDPE), polystyrene (PS), and polyethylene glycol (PEG) were used to represent MPs with no functional groups, aromatic groups, and ether groups, respectively. Co-pyrolysis of cellulose and one of these MPs were conducted. For experiments of HDPE/cellulose pyrolysis, different thickness of HDPE layers was coated on top of the cellulose. For PS/cellulose and PEG/cellulose pyrolysis, the polymer and cellulose fractions were homogeneously mixed before the experiments. All products were analyzed by gas chromatography (GC) techniques.

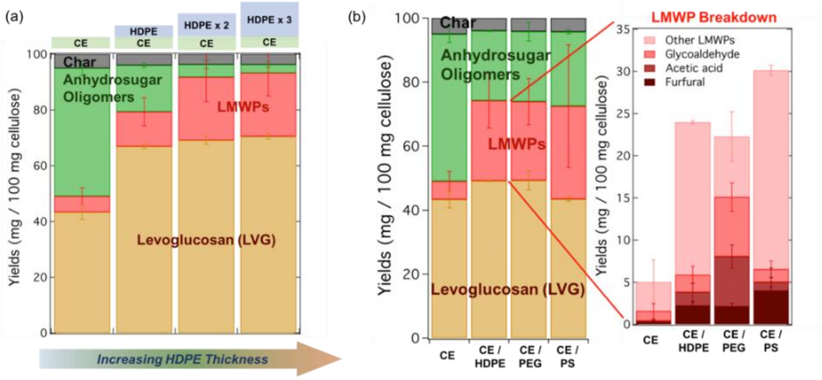

Figure 4: (a) Thicker high-density polyethylene (HDPE) layers on top of cellulose (CE) thin-films led to higher yields of LVG and LMWPs after fast pyrolysis; (b) the addition of PEG and PS in cellulose pyrolysis promotes the yields of acetic acid, glycoaldehyde, and furfural.

Figure 1(a) shows the effects of physical inhibition caused by MPs on product yields from cellulose pyrolysis. Specifically, thicker HDPE layers above cellulose led to higher levoglucosan (LVG) and lower molecular weight product (LMWP) yields. The results can be explained by the fact that larger anhydrosugar oligomers and aerosols are trapped in the MP phase, where these compounds decompose into LVG and glucose-derived LMWPs. These experimental results support the hypothesis that MPs physically inhibit product escape. Figure 1(b) shows that LVG and LMWP yields both increased in CE/HDPE pyrolysis compared to neat CE pyrolysis, likely due to the aforementioned physical inhibition effects. The yields of LVG and total LMWPs are similar in CE/HDPE and CE/PEG pyrolysis. However, individual LMWP yields are different, where the yields of small (C_1–C_3) products (glycoaldehyde and acetic acid) are higher in CE/PEG pyrolysis, suggesting that ether moieties in PEG inhibit glucose dehydration, promoting retro-aldol fragmentation. The CE/PS mixtures gives the highest LMWP yields and the lowest LVG yields, suggesting that aromatic moieties in PS inhibit glycosidic bond cleavage. The yield of furfural, an important value-added chemical, increased over an order of magnitude.In summery, it was found in cellulose fast pyrolysis in the presence of MPs that HDPE layers inhibit evaporation of anhydrosugar oligomers, while aromatic and ether groups of PS and PEG inhibit glycosidic bond cleavage and dehydration reactions via hydrogen bond stabilization. Our work suggests that MPs that melt at high temperatures and have degradation timescales longer than that of biomass can potentially be used as inhibitors to selectively promote the yields of key value-added chemicals.

CO2 PARTICIPATION IN CROSS-LINKING REACTIONS AND CHAR FORMATION DURING BIO-OIL PYROLYSIS.

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Key Words: Cross-Linking, Biooil, Pyrolysis, Char

The integration of new CO2 capture and storage technologies into energy generation processes has led to the development and study of the oxy-fuel combustion, in which the nitrogen in the air is replaced by recirculated CO2 that facilitates its capture and storage to reduce polluting emissions. Currently, the integration of oxy-fuel technologies with the use of new fuels such as bio-oil obtained from the pyrolysis of biomass is a topic of interest. In this case, the CO2 content surrounding the bio-oil droplets modifies the pyrolysis mechanism due to barriers in the diffusion of light volatiles at low temperatures (less than 200°C) and formation of char as a result of the cross-linking reactions [1] explained by the hydrolysis of the heavy fraction of bio-oil is restricted in this atmosphere.

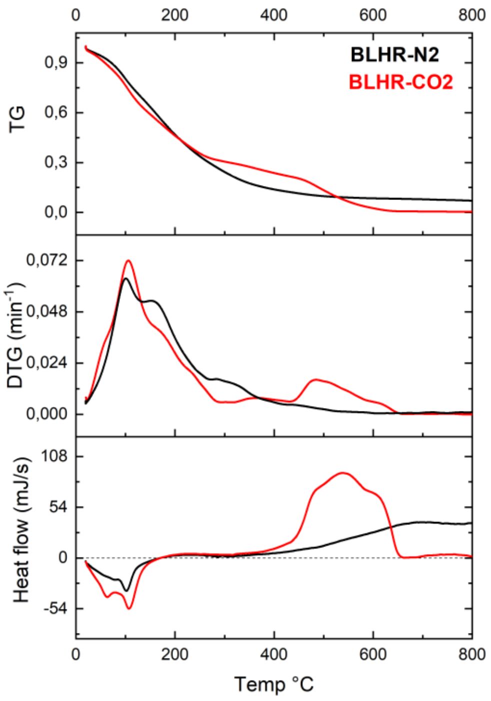

Figure 5 – BioOil Low Heating Rate (BLHR) pyrolysis in N2 y CO2 Atmospheres

The thermal decomposition of bio-oil in the atmosphere of N2 and CO2 presents significant differences. At temperatures between 400°C and 700°C in a CO2 atmosphere, there is evidence of the carbonization because of the cross-linking reactions. Char samples were obtained before (400 °C) and after (700 °C) of the cross-linking reactions and their chemical characteristics were analyzed using FTIR, Reactivity Analysis and Elemental Analysis[2], which permitted to elucidate the role of CO2 in carbonization.

It was found that the destruction of functional groups corresponding to the oligomers of lignin present in the bio-oil are strongly influenced when the process is carried out in N2[3], while in CO2 atmospheres the functional groups remained in char after carbonization processes. This could be explained because the diffusive phenomena of the volatile fractions and the exit water generated during the hydrolysis processes is restricted by CO2 presence. Then, CO2 carbonization will improve chemical characteristics of char obtained both in quality and quantity respect to the N2 carbonization.

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SYNERGISTIC EFFECTS OF BIMETALLIC Mo-W CARBIDE IN HYDRODEOXYGENATION OF GUAIACOL

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Key Words: synergistic effect; bimetallic Mo-W carbide; hydrodeoxygenation of quaiacol; DFT calculations; mechanistic investigation

Bimetallic MO-W carbide was synthesized via temperature-programmed reduction to generate a β-Mo_2C like phase with bulk morphology in order to investigate the synergistic effects of a combination of molybdenum and tungsten in carbide. The solid was characterized using X-ray diffraction (XRD), N_2 physisorption, X-ray photoelectron spectroscopy (XPS), H_2-chemisorption, and ammonia temperature programmed desorption (TPD-NH_3). The bimetallic carbide exhibited a significantly higher density of H_2-activating sites than the corresponding monometallic carbides prepared using the same method. In the HDO of guaiacol at 350°C, MoWC yielded the highest hydrodeoxygenation (HDO) catalytic activity and produced completely deoxygenated products with a selectivity of 92 mol% in which benzene selectivity was 70 mol%. The superior catalytic activity is attributed to the presence of both H_2-activating sites and oxophilic sites. Under the testing conditions, HDO of guaiacol over monometallic molybdenum carbide followed both direct deoxygenation (DDO) and hydrogenation-dehydration (HYD) pathways, while MoWC strongly favored the DDO route. The catalyst remained highly stable over 8h on stream.

The electronic interaction between Mo and W in MoWC and their effect on the energetics and mechanism of guaiacol HDO was further explored using first principles Density Functional Theory (DFT) calculations. Our calculations showed that oxygen bonded ~ 1 eV stronger on the bimetallic carbide (MoWC) than on the monometallic molybdenum carbide surface, confirming the enhanced oxophillicity of W in the presence of Mo, in agreement with XPS studies. The observed preferential selectivity towards deoxygenated products on MoWC surfaces was further explained by the mechanistic investigation on MoWC and monometallic molybdenum carbide surfaces. Our calculations showed that the DDO pathway was kinetically favored on the bimetallic MoWC surface (leading to benzene), while the HYD and DDO pathways proceeded with competitive barriers on monometallic molybdenum carbide (leading to both cyclohexene and benzene).

FEEDSTOCK BLENDING AS A STRATEGY FOR HYDROTHERMAL LIQUEFACTION: LIPID-RICH SCUM FROM PRIMARY SEDIMENTATION AND WASTEWATER SLUDGE

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Key Words: hydrothermal liquefaction, wastewater sludge, scum, FOG

One salient advantage of hydrothermal liquefaction (HTL) is the ability to process diverse feedstocks individually or as blends. This creates an opportunity for using wet organic waste feedstocks that in many cases pose a disposal liability. The low cost associated with the feedstock enables cost-effective deployment of smaller, decentralized processing plants that match the geographic availability of wet waste resources. Two underutilized sources of wet waste biomass are wastewater sludge and fats, oils, and greases (FOG). In the United States, these each represent about 20% of the total HTL biocrude production potential from wet wastes. In this study, the selected FOG stream is decanted scum from the primary sedimentation operation of the same wastewater treatment plant (WWTP) that provided the sludge.

Among the types of FOG, wastewater scum is one of the more complex and challenging. Scum contains entrained water, plant matter like leaves and seeds, and bits of garbage (paper and plastic). For most other processes to access the lipids in scum, some combination of heating, filtering, and solvent extraction would be required, leading to costly and/or inefficient recovery. HTL is preferable because it is a wet process and the scum can be blended directly to capture the whole energy content in the blended feed.

Using a blend of primary and secondary sludge from Central Contra Costa Sanitary District (CCCSD) and decanted scum from CCCSD primary sedimentation as the source of FOG, a blend of sludge and scum was successfully prepared and processed in a bench scale continuous flow HTL system. A total of 54 L of blended slurry was converted to 4.2 L of biocrude oil. The scum was blended with the sludge such that it represented 20 wt% of the total dry, ash-free (daf) solids in the feed. The resulting biocrude had a much lower density (0.95 g/cm^3) than the biocrude from CCCSD sludge alone (0.99 g/cm^3) leading to improved gravity separation from the aqueous phase. The biocrude was also lower in moisture.

During the oral presentation, the focus will be on the process of feedstock selection, evaluation, and characteristics including detailed steps and equipment used to format the blended feedstock for use in the HTL reactor system. The poster will include data for the integrated process including mass balance, yields, and characterization of products.

PYROLYSIS OF PLASTIC WASTE: OPPORTUNITIES AND CHALLENGES

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ANAEROBIC DIGESTION OF THE AQUEOUS PYROLYSIS CONDENSATE

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Key Words: Aqueous pyrolysis condensate, anaerobic digestion, pyrolysis, biochar, methane

Fractional condensation of biomass pyrolysis vapors allows the segregation of different pyrolysis fractions and a separation of an aqueous pyrolysis condensate from an organic rich dry bio-oil fraction. Aqueous pyrolysis condensate is often referred at as “wood vinegar” or “pyroligneous acid” since it contains 70-80% water together with 10-20% acetic acid, and smaller quantities of acetone and methanol mixed with hundreds of other chemicals in small concentrations. Such aqueous pyrolysis condensate cannot be easily disposed of, and it may represent a valuable resource. For example, the significant percentage of acetic acid offers the opportunity to attempt its conversion into methane by anaerobic digestion.

Aqueous pyrolysis condensate produced by fractional condensation of vapors generated from the pyrolysis of birch bark at 500 °C has been characterized (elemental composition, pH, COD, volatile fatty acids (particularly acetic acid), ammonia, hydrogen sulfide, minerals, and phenolics), inoculated with a consortium of bacteria from an organic waste anaerobic digestor, and digested over several weeks. Biogas production has been progressively monitored and methane and CO_2 concentrations experimentally measured.

We performed a large number of experiments to investigate the effects of (a) dilution of the aqueous pyrolysis condensate, (b) nutrients addition, and (c) addition of bio-char on the production of biogas and on its methane concentration.

The results clearly show that the anaerobic digestion of aqueous pyrolysis condensate is possible and leads to the production of biogas and on the reduction of the COD of the original feedstock to make it suitable for disposal. However, the high phenolic content of the condensate, together with possibly other chemical species, creates considerable inhibition of microbial methane production. Such inhibitory effects, however, can be mitigated by gradual adaptation of the bacteria population to the feedstock composition. The result show that 50 to 60 days are required before significant biogas production is observed when raw anaerobic pyrolysis condensate is processed. The addition of bio-char to the process is beneficial in shortening the lag phase to approximately 20 days and is triggering a higher volume of biogas production with an increased methane content, compared to similar conditions without bio-char. This is attributed to the ability of bio-char to adsorb inhibitory compounds as well as to create more favorable environmental conditions for the digestion process. Similarly, but less effectively, the addition of selected nutrients is shown to benefit the anaerobic process by shortening the lag phase to 40 days.

THERMOLYSIS OF PLASTIC WASTE- OPPORTUNITIES AND CHALLENGES

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Key Words: Plastic waste, Pyrolysis, Petrochemicals, Co-feeding, Wax

Plastic waste offers an attractive business opportunity if treated intelligently. Presently, owing to the lack of economically viable recycling solutions and political interest, this valuable feedstock is bound for an ill-fated destiny i.e. landfills and inefficient incineration. Landfilling plastic waste is rather a storage mechanism than a prevention mechanism. Plastics can stay in ground and in oceans for hundreds of years without decomposing, posing serious environmental hazards. Given the complexity of the plastic waste mixture and heterogeneity of waste streams, a single recycling solution is improbable; however, the current environmental situation demands an urgent need to find ways to tackle this ever-growing waste problem.

Thermolysis (pyrolysis) of non-recyclable plastic waste allows the waste to be converted to a valuable hydrocarbon rich petrochemical-based feedstock. This feedstock i.e. composed of oil, wax and gas, has great potential to be used in multiple applications, one of the most attractive ones is co-feeding in a refinery. The gas and char generated in the process can be used to provide the energy needed for thermolysis. Thermolysis of plastic waste has to offer many benefits over other recycling techniques such as the recycling of feedstock contaminated with dirt and organics, recycling of problematic waste such as laminates, multilayer plastic and even hazardous plastics such as those found in electrical or demolition waste. Furthermore, it converts the solid waste that is difficult to store, transport and dispose, into liquid and wax product that is easily transportable. However, like other recycling technologies, it also suffers from some technical challenges, which should be scrutinized before choosing the recycling technology. From the practical aspects, the choice and availability of feedstock, reactor type and investments, use of a catalyst, products needed, availability of standards, REACH, and established markets etc. all these factors come into play and should be evaluated thoroughly. This presentation targets the role of thermolysis in managing global plastic waste. Technological challenges associated with reactor types used for thermolysis and the quality and upgrading of products will be discussed, i.e. comparison of the slow vs. fast thermolysis. Furthermore, the results of a national ‘Waste to Products’ project will be presented including the learnings from thermolysis experiments.

COMPARISONS AMONG TECHNICAL AND MILLED WOOD LIGNINS THROUGH PRINCIPAL COMPONENT ANALYSIS OF FTIR SPECTRA

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Key Words: biorefinery, lignin, FTIR, characterization, principal component analysis

With the growth of biomass processing in biorefineries, there is an increasing need to develop rapid and simple methods for biomass characterization. One important component of biomass that is of signification interest in pyrolysis and liquefaction research is lignin, which is the world's predominant source of renewable aromatic carbon. Due to its complex, heterogeneous nature and distinct variations among different biomass feedstocks, the characterization of lignins presents a unique challenge. In this study, we will show that clear divisions and comparisons can be made among a variety of lignins based on their FTIR spectra quantitatively assessed through principal component analysis (PCA). The eight lignins so far characterized are: two varieties of softwood kraft, one hardwood kraft, corn stover milled wood lignin (MWL), Douglas fir MWL, hybrid poplar MWL, wheat straw soda, and wheat straw organosolv. These samples were analyzed using a Bruker Alpha FTIR-ATR instrument (in addition to other characterization techniques). The spectra were baseline corrected and normalized, and the intensities of 15 peaks were recorded. The 15 spectral peaks were chosen based on previous work published by Li and McDonald (*Industrial Crops and Products*, 62, 2014, 67-76). PCA and data visualization was done using Python in the Jupyter Notebook environment.

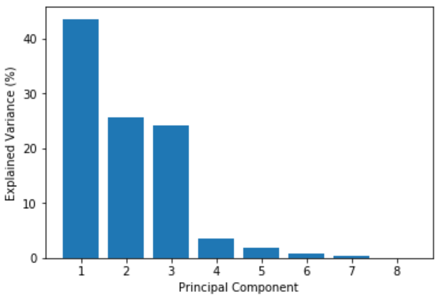

Fig. 6: Explained Variance of Each PC

Principal component analysis revealed that among the eight lignins, they can be qualitatively grouped based on both their feedstock variety (*e.g.,* hardwood, softwood) and isolation method (*i.e.*, kraft, MWL, soda, organosolv). Quantification of the explained variances for each principal component (PC) suggests that three PC's are necessary to capture over 90% of the variation among the samples (Figure 1). The principal component plots (Figure 2) show that softwood kraft lignins are clustered, corn stover and Douglas fir MWLs are clustered, and hardwood kraft and wheat straw soda are clustered. The two wheat straw and two hardwood samples tend to have positive values for PC1, while the softwoods and corn stover are negative. The MWLs are closely grouped along PC2, and the organosolv wheat straw is uniquely large along PC3. Depending on which of the three PC plots are assessed, other possible groupings can be reasonably drawn, suggesting that the FTIR spectral characteristics of lignins are distinctly affected by both their original biomass feedstock and isolation or extraction method. The analysis of FTIR spectra with PCA is a simple and efficient way to quickly assess the characteristics of an unknown or poorly-understood lignin sample, based on its comparison with other well-studied lignins. Previous work has shown that PCA is a robust technique for analyzing bio-oil MS data (Jia, et al., *Energy & Fuels*, 29, 2015, 7364-7374; Pattiya, et al., *Fuel*, 89(1), 2010, 244-253), and this work shows that such analysis can easily be extended to FTIR spectra of contrasting lignins. Continuing research will further assess the FTIR data for other important characteristics (both qualitative and quantitative), as well as to include additional technical lignins in the analyses.

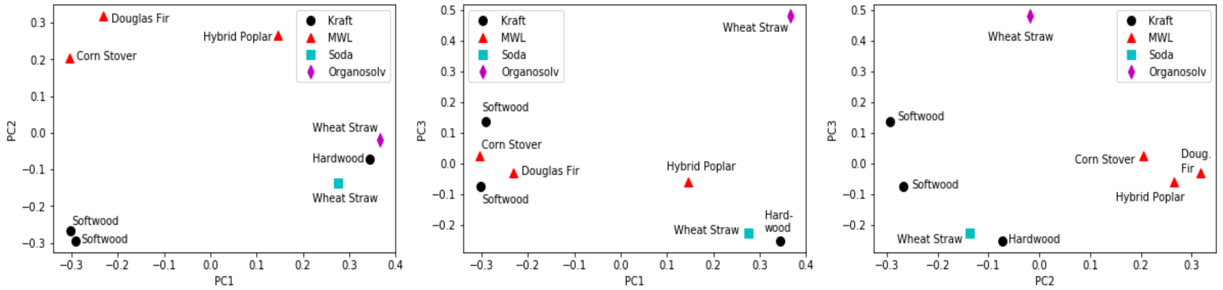

Figure 7: PCA of lignin FTIR (PC1 vs. PC2, PC1 vs. PC3, and PC2 vs. PC3)

HYDROTHERMAL LIQUEFACTION OF ORGANIC WASTE STREAMS ON A CONTINUOUS PILOT SCALE REACTOR

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Key Words: hydrothermal, liquefaction, bio-crude, sewage sludge, waste, hydrotreatment

Hydrothermal liquefaction (HTL) is a promising technology for biofuel production and treatment of organic wastes and biomass. Due to the wet nature of the process where biomass is heated in an aqueous slurry at 350°C and 200 bar, wet biomass and wet wastes are particularly suited for the process. The current study investigates the utilization of wastewater treatment sludges and other organic wastes for the production of sustainable petroleum replacement products. The work has been carried out on a pilot scale continuous hydrothermal liquefaction reactor with a novel oscillating flow system and heat exchanger. The influence of these are discussed in terms of heat recovery and operability of the plant. The reactor was run at 50 L/h with maximum solids loadings of ~25% and short residence times of <15 minutes. Once steady state operation was achieved a heat recovery of over 80% was accomplished, leading to an energy efficient process. During operation of the HTL system, approximately 5 units of energy are created in the form of bio-crude for every unit of energy invested for heating and pumping the slurry (EROI>5). We present and discuss the results of processing diverse samples ranging from high ash (sewage sludge), lignocellulosics (miscanthus) and manure to microalgae. The potential of mixing different waste biomasses such as sludge and lignocellulosics, plastics and lignocellulosics is explored during this research and synergistic effects on bio-crude yields and fuel quality are observed, leading to higher carbon and energy recoveries. Water phase recycling of the HTL process water was employed during the liquefaction of pine where a significant increase in bio-crude yields, energy recovery and energy return on investment could be achieved. Initial results on bio-crude upgrading via catalytic hydrotreatment are also presented, demonstrating the feasibility of the HTL process as a viable pathway towards drop in replacement fuels. The current presentation gives a realistic insight into the processing of diverse biomass feedstocks at pilot scale, showing the potential of the technology while areas for future development and bottlenecks are highlighted.

EN-FUELS FROM SOLID WASTE BIOMASS BY THERMO-CATALYTIC REFORMING

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Key Words: Thermo-catalytic Reforming, Biomass Conversion, EN-Fuels.

Intermediate pyrolysis describes a process of converting feedstock by heating it up in the absence of oxygen under moderate, “intermediate” conditions. Typical conditions are a residence time for solids between 5 to 30 minutes, low heating rates and temperatures between 350 °C - 450 °C. Due to these conditions intermediate pyrolysis has remarkable advantages regarding the feedstock, compared to other processes based on flash pyrolysis. Large particles, like pellets or chips can be used. Dry matter content can be below 50% from a technical point of view. For economic reasons the dry matter should be more than 70 % to avoid using energy mainly for drying. However, this dry matter is still very low compared to the requirements of most flash pyrolysis reactors. Another advantage is the use of variable and heterogeneous feedstock, preferably residue and waste biomass. The feedstock can vary from agricultural residues, biogas digestate, municipal and industrial biowaste to sewage sludge. The latest development of the intermediate pyrolysis technology is Fraunhofer UMSICHT´s Thermo-Catalytic Reforming process (TCR®). It is a novel process for the production of char, gas, and bio-oils with improved properties.

One significant innovation of TCR® is the integrated downstream catalytic reforming step. This multi-patented technology enables the high quality of the final products carbonisate, syngas, and oil. The robustness of the process permits the utilization of various biogenic feedstocks. The yield of the products depends on the chemical properties of the feedstocks, whereas the quality and characteristics of the products are due the robustness of the process, largely independent of the feedstocks. With the focus on the TCR® oil there is one unique selling point: The oil is thermally stable and therefore distillable. This is the basis for other thermal upgrading processes like e.g. hydro-treatment. Furthermore, the thermal stability of the TCR® oil is a basic prerequisite for usage in the fossil petrol processing industry. This includes, among other applications, combined heat and power (CHP) plants. Additional unique properties are the low water content, the low total acid number, and the high heating value. The high quality of the crude TCR®-oil can be further improved to EN fuel quality by distillation and hydrodeoxygenation (HDO). For hydrodeoxygenation sulfonated NiMo catalyst at temperatures of around 370 °C and a pressures in the range of 140 bar and with LHSV of 0.3 per hour were applied. The resulting products showed full properties of standard hydrocarbon fuels. A separation into diesel and petrol fraction by rectification demonstrated, that both fractions met the fossil fuel standards (EN 228 and EN 590). Through hydrotreating the hydrogen content was increased and the oxygen, sulphur and nitrogen content was significant lowered or respectively removed in an efficient way with a yield over 85 %.

The fuel has been tested by a Volkswagen XL 1 car under real road condition for several hundred kilometres with an average diesel consumption of 1.3 litres per 100 km.

The TCR technology has been tested and applied in laboratory scale (2kg/h throughput) and pilot scale (30 kg/h throughput). In the frame of a Horizon 2020 demonstration project a TCR 500 (500kg/h throughput) integrated with a hydrogenation unit is now being constructed and will be in commissioning beginning of 2020.

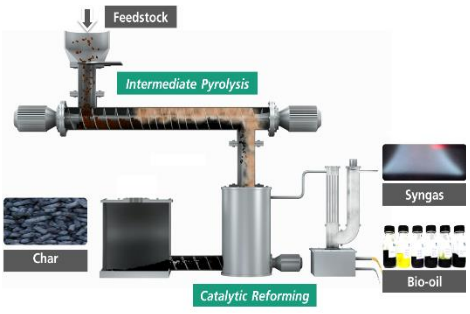

Figure 1. Scheme of TCR-reactor

Figure 2: TCR crude and hydrogenated TCR fuel

CELLULOSE VALORIZATION IN BIOREFINERY: INTEGRATION OF FAST PYROLYSIS AND FERMENTATION FOR BUILDING BLOCKS PRODUCTION

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Key Words: Cellulose, biorefinery, pyrolysis, fermentation, building blocks

A combination of thermochemical and biological conversion of cellulosic materials is a promising alternative for the production of biofuels and building blocks in an integrated biorefinery. Indeed, enzymatic depolymerization is selective but slow and expensive. It would be of interest to associate thermochemical conversion for a fast depolymerization of biomass with biochemical conversion for a selective conversion of depolymerized liquid streams. In this work, cellulose is pyrolyzed to produce sugars that can be used as substrate for a fermentation process. This work is the result of a scientific collaboration between ICFAR (London, Canada) and CNRS (Nancy, France).

Pyrolysis was performed in a fluidized bed reactor at 475^{o}C with a bio-oil yield of 73.4 wt.% (Figure 1). Different fractions of bio-oil were recovered with a set of 5 condensers. Levoglucosan and total sugars were quantified by GC-FID-MS and phenol/sulphuric acid method respectively. The maximum yields of levoglucosan (43.7 %) and total sugars (80.4 %) were found in the first condenser that was kept at 70^{o}C.

Due to the non-fermentable condition of levoglucosan, all the oil fractions, as well as a mixture of them, were hydrolyzed to obtain fermentable glucose. The different bio-oil fractions and a mixture of all fractions were used as substrate in a fermentation reactor to produce acetone, butanol and ethanol (ABE). The talk will present the mass yields obtained for the integrated process combining pyrolysis, hydrolysis and fermentation (figure 2).
The microorganisms were not able to grow in the mixture of all fractions. On the contrary, fractions from condenser 1 and 2 lead to normal bacterial growth and fermentation products pattern. Maximum yields (per gram of oil) of acetone=4.6 %, butanol=13.2 % and ethanol=0.1 % were found for the bio-oil collected in the first condenser. These results put in evidence the importance of pyrolysis with staged condensation as an entry for fermentation processes.
The methodology proposed in this work could be applied to other biochemical conversion of bio-oils to produce higher added-value products.

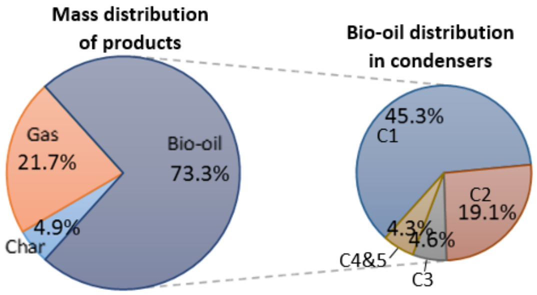
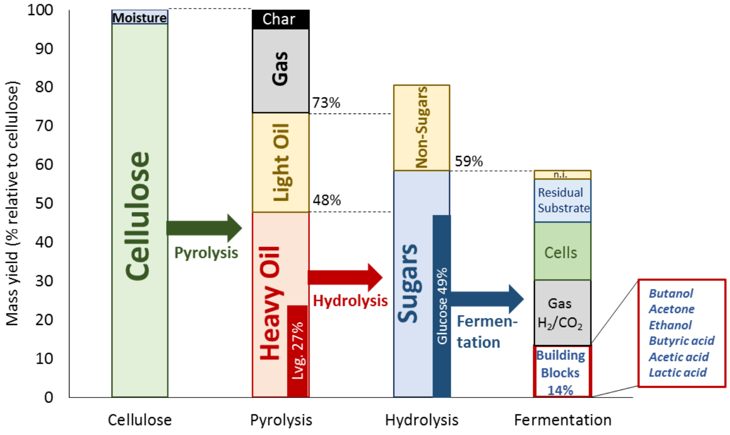


Figure 2. Fate of cellulose and its products along the integrated process including pyrolysis, hydrolysis and fermentation

Figure 1. Product distribution of cellulose pyrolysis and condenser mass fractions of bio-oil. C=Condenser. C1=70^{o}C, C2=45^{o}C, C3, C4&5=5^{o}C.



ABLATIVE FAST PYROLYSIS OF BIOMASS - A NEW DEMONSTRATION PROJECT IN CALIFORNIA, USA

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Key Words: fast pyrolysis, ablative pyrolysis, bio-oil, pilot plant

California is the fifth largest economy in the world and has about 40 million inhabitants. The California federal government has decided to stick to the Paris climate change agreement by 2030. For many years, California has been feeling the effects of global warming caused by the largest tree extinction in modern history, a five-year dry spell and resulting bark beetle plague, and severe forest fires coupled with heavy winds, heavy rains, and rising sea levels. California is therefore promoting the use of biogenic fuels in the transport sector. In spring 2017, there was a grant funding opportunity from the California Energy Commission (CEC) in the program: "Research and Demonstration to Decarbonize Transportation Fuels". Funding supported innovative processes for production of bio-intermediate fuels. to be further used for the generation of sustainable low-carbon fungible biofuels in California's transport sector. In order to meet the given budget, a modular pyrolysis system with an ablative reactor was proposed by the authors. The advantage over fluidized bed processes lies in the better space-time yield, i.e. the systems can be kept small and fit in standardized shipping containers, since neither a fluid heat carrier nor a cycle gas is needed. After careful consideration of the submitted project proposals, our concept was considered worthy of support so that in October 2018 the contracts could be signed. The project duration is 3.5 years. The American business partner is Biogas Energy, Richmond, CA. According to the contract, the pyrolysis plant must produce at least 50,000 gallons (about 190,000 L) of bio-oil. At the beginning of the 21st century, there were two patents on ablative fast pyrolysis reactors. On the one hand the BtO process of PYTEC GmbH, Hamburg with a disk reactor (Fig. 1a), on the other hand the drum reactor, consisting of stator and rotor, Aston University, Birmingham, UK (Figs. 1b, c). In both systems wood chips are pressed against a hot, rotating surface (about 600 ° C) of the reactor. While the disk reactor of PYTEC needs a complex, multiple feeder system which was implemented in a pilot plant with a capacity of 250 kg/h, the drum reactor comes with a conventional two-stage lock hopper system, since only in the reactor the wood chips are being pressed between the walls of the stator and the rotor using a special blade system. The latter fast pyrolysis reactor system was brought to pilot maturity in recent years by Energolesprom (ELP), Kazan, RU and is now being used after some modifications in California. The plant, with a throughput of 500 kg/h, will be built on the site of Western Place Management Authorities close to Sacramento. Expected start of operation is summer 2020. For start-up demolition wood will be the preferred feedstock. Later on biomass from forestry and agriculture will be processed.

Figure 1a Ablative disk reactor

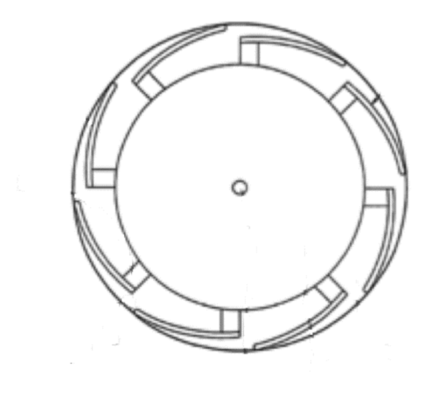

Figure 1b Ablative drum reactor (cross section)

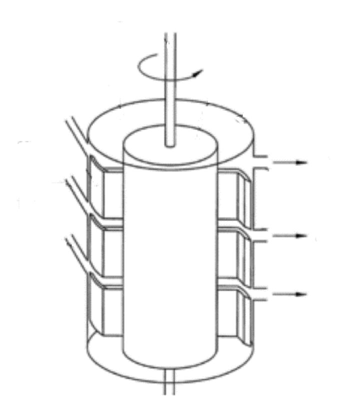

Figure 1c Ablative drum reactor (longitudinal section)

FAST PYROLYSIS BIO-OIL PRODUCTION IN A ENTRAINED FLOW REACTOR PILOT

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Key Words: Pyrolysis / Bio-oil / Combustion

Bio-oil produced from biomass fast pyrolysis could constitute an alternative to fossil liquid fuels, especially to be combusted for local district heating. So far, only few studies have dealt with bio-oil production by biomass fast pyrolysis in an entrained flow reactor [1], yet it could constitute an alternative to the better-known fluidised bed pyrolysis process.

In the context of the BOIL project with the CCIAG Company (Grenoble district heating), a new pilot based on an entrained flow reactor concept has been designed [2]. The pilot design has been carried out on the basis of woody biomass fast pyrolysis experiments and modeling performed in a drop tube reactor as a first step laboratory-scale study, and also CFD modeling [2-3].

The facility is composed of a biomass injection system with a hopper and a feeding screw, an electrically heated pyrolysis reactor, a cyclone to separate gas and char, 3 heat exchangers to cool the gas (at 30°C, 0°C and 0°C respectively) and condense bio-oil, and a post-combustion unit to burn the incondensable species. Gas temperature is maintained at 350°C from the reactor outlet to the entrance of the first heat exchanger in order to avoid bio-oil condensation.

Several conditions were tested in 14 runs: 3 different biomass feedstocks, varying biomass feeding rates from 2 to 9 kg/h and two reactor temperatures 500°C and 550°C. 85 kg of bio-oil has been produced for combustion tests. Recovered bio-oil mass yield is on average 50%, its LHV is about 15 MJ/kg, its water content 26%w and its pH 2.15. We identified three main difficulties during the runs: about 15% of the bio-oil go through the heat exchanger, some char particles go through the cyclone which causes regular plugging of the first heat exchanger. Detailed analyses of the bio-oil produced have been done and the chemical and physical bio-oil characteristics have been compared to the European Standard recommendations [4].

With a regularly cleaning of the first heat exchanger, we successfully produce bio-oil with physical and chemical properties in agreement with the European Standard recommendations.

Combustion tests of the bio-oil produced have been carried on by the CIRAD. They succeeded in obtaining a stable flame (without the use of a pilot flame) in a 50 kW burner and a 250 kW combustion chamber. However the physical and chemical characteristics of the bio-oil involve the use of specific pump and pulverization system adapted.

In perspective for future projects, it would be interesting to perform pilot modifications in order to increase bio-oil yield and to minimize heat exchanger cleaning, and to test other resources like agricultural biomass or solid recovered fuels.

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LAMBIOTTE, PREMERY, FRANCE: AN INDUSTRIAL PYROLYSIS BIOREFINERY OPERATED DURING 120 YEARS

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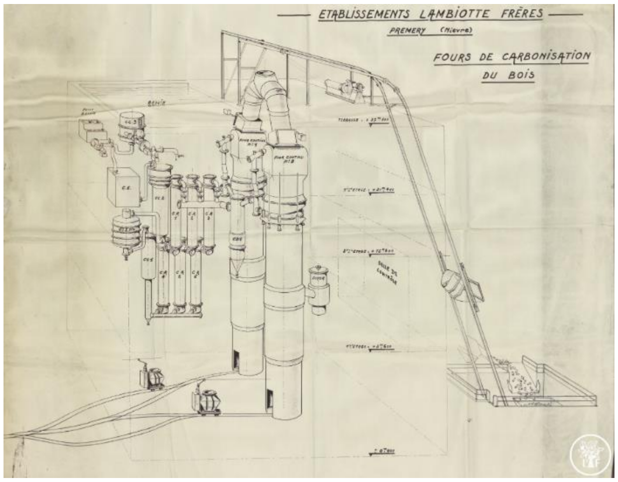
Key Words: biorefinery, pyrolysis, industrial development, purification

The Lambiotte process is a well-known process for the continuous carbonization of wood. It is also sometimes called as the “CISR” process which is still in operation in Belgium, France, etc. [1, 2]. But this process is the small and simplified “son” of a much more advanced process (sometimes called as “SIFIC”) developed by the Lambiotte company in France (in Premery). The CISR reactor is smaller than the SIFIC one and burns the condensable products to produce mainly char. The SIFIC process was an integrated forest-refinery. It was operated in Premery to produce about 20000 tons per year of char from about 100000-120000 tons of wet wood (~45% moisture content, before drying in mobile vertical beds) but also to produce various chemicals from the carbonization bio-oils. The carbonization oil was fractionated and purified in an advanced process combining solvent extraction, distillation (more than 40 distillation columns) and catalytic reactions. In the beginning of the 20th century, the factory was able to produce: methanol, formol and their derivatives, acetates and solvent (from acetic acid), creosote, guaiacol, (wood) pitch, various medicines (such as antiseptics). Then even food aromas have been produced.

This talk will present the historical development of this industry from 1886 to its end in 2002 based on our perusal of old (unpublished) manuscripts. We will present the technological development, from batch retort to the continuous mobile bed process (invited by Charles Coutor) and implemented in 1947. We will discuss the main process units and the industrial mass and energy balances. For instance, in 1981, the products were: 20000tons of char, 3000t of acetic acid, 100t of formic acid, 1200t of “methylene” (methanol with impurities), 1000 t of sodium acetate, 200t of various solvents, 80t of tanning products, 14t of methylcyclopentenolone (caramel and licorice aroma for coffee and tobacco), 2t of maltol (wild strawberry aroma), 15t of diacetyl (butter aroma for margarine) and propionic acid (additive for biscuits), etc.

This factory has employed more than 300 people and brought important economical and social profits as the main industry of the rural area of Premery. But this industry has also led to important environmental impacts (air, soil and water pollution). We will conclude on our (personal) analysis of the success and decline of this industry. This story may help us to build a sustainable forest-based industry.



Lay out (1964) of the carbonization process presenting the 2 vertical moving beds in parallel (installed in 1947 and 1953) and part of the condensation system of bio-oil

A human story

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PARAMETRIC STUDY OF LAB-SCALE AND PILOT-SCALE BIOMASS TORREFACTION FOR THE PRODUCTION OF WOODSTOVE BRIQUETTES

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Keywords: Torrefaction; Olive stones; Briquettes; Woodstoves; Emissions.

Conversion of torrefied olive residues to high-density briquettes is a potential solution to solid waste problems as well as to the lack of locally available fuel wood in Ireland. In this study, olive stones were torrefied at various temperatures and holding times in a fixed-bed reactor. Effects of process parameters such as heat treatment temperature from 200 to 300℃, residence time from 30 to 60 min, and particle size from 0.18 to 3 mm on the yield and composition of products were investigated and the results were compared with the mass balances from industrial-scale torrefaction plant at the Arigna Fuels (Carrick-on-Shannon, Ireland). The olive stones of larger particle size produced more liquid and gaseous products than smaller particles in a fixed bed reactor, whereas particle size had significantly less influence on the product yields than residence time and heat treatment temperature. The analysis of liquid products of the industrial-scale plant showed a greater content of heavy molecular products compared to the lab-scale pyrolysis using high-performance liquid chromatography and size exclusion chromatography techniques. New value-added products were developed from the tar compounds produced at the industrial-scale torrefaction plant. In addition, the lab-scale experiments showed that the ash content of torrefied biomass significantly increased with the increased feedstock particle size. The torrefied olive stones briquettes using different binders were tested in a conventional woodstove. Torrefaction of olive stones has been found to reduce the emissions by approximately 60% compared to the non-treated feedstock. This demonstrates that torrefaction has good potential as a cost-effective and sustainable process for the production of woodstove briquettes from low-quality feedstocks.

CATALYTIC PYROLYSIS

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SCALABLE PROCESSING CONCEPTS FOR MICROWAVE PYROLYSIS

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Key Words: Microwave, Pyrolysis, Biochemicals.

Microwave pyrolysis of biomass has long been recognised to provide potential opportunities for producing a range of bio-based products. Unlike conventional heating, microwave heating occurs through the interaction of biomass with electromagnetic energy, with the biomass heated volumetrically by energy conversion instead of conventional heat transfer mechanisms. With microwave heating pyrolysis can be achieved within a cold surrounding environment, a feat that is not possible with conventional heating processes. This unique phenomenon presents a number of opportunities for processing of biomass feedstocks, which include enhanced product quality and a significantly simplified process flowsheet, both of which improve the economic viability of industrial biomass processing. Examples of the benefits of microwave heating include the elimination of size-reduction and particulate removal steps, and simplification of inert-gas preparation and recycling systems. These are discussed within the paper, along with the enhanced product quality that can be produced as a result.

Previous studies in this field have typically made use of fixed bed reactors, in which heating heterogeneity issues and undesired thermal runaway of the biomass are inherent. This paper presents five alternative and scalable microwave processing concepts which have already proven to successfully operate at scale, within an industrial environment. The potential application of these concepts for biomass processing, and their ability to deliver a step-change in product quality and flowsheet simplification is discussed within the paper.

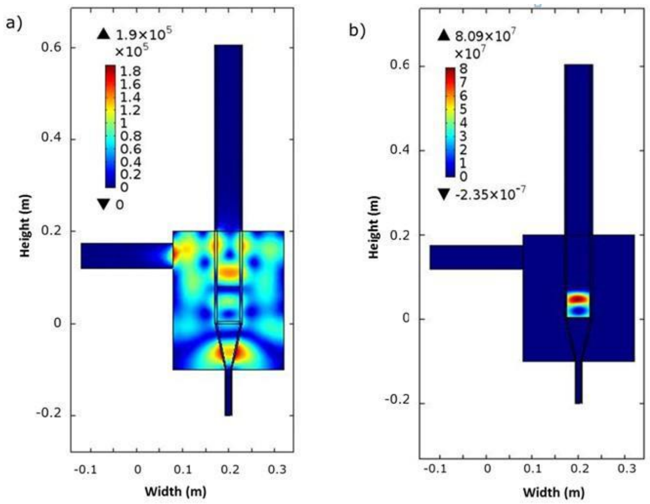

Figure 8 – Electric Field and Power Density in a microwave fluidized bed

TERNARY SYSTEM OF PYROLYTIC LIGNIN, MIXED SOLVENT, AND WATER: PHASE DIAGRAM AND IMPLICATIONS

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Key Words: bio-oil; pyrolytic lignin; phase diagram; solubility

Bio-oil from biomass fast pyrolysis is considered to be an important feedstock for the production of renewable fuels and green chemicals. Fast pyrolysis bio-oil generally contains a water-soluble fraction (excluding water), a water-insoluble fraction (i.e., pyrolytic lignin, PL), and water in a single phase. However, phase separation can occur during bio-oil transport, storage, and processing. In this study, a mixed solvent (MS) is developed based on the compositions of various fast pyrolysis bio-oils produced from a wide range of feedstocks and reactor systems. Experiments are then carried out to investigate the phase behavior of the PL/MS/water ternary system. Several ternary phase diagrams are constructed for PL and its fractions, and the PL solubilities in various MS/water mixtures are also estimated. Under the experimental conditions, the PL solubility in the MS is high, i.e., ~112 g per 100 g of MS. In the PL/MS/water system, an increase in water content to ~17 wt % in the MS/water mixture leads to a slight increase in the PL solubility to a maximal value of ~118 g per 100 g of MS/water mixture, followed by a gradual decrease in the PL solubility when the water content further increases. It is found that the phase stability of the PL/MS/ water system is strongly determined by the composition of the system. For example, the PL/MS/water system is always stable when the MS content is >50 wt %, while the system is always phase-separated when the PL content is >54 wt %. A comparison of the results for various PL fractions indicates that the molecular weight of PL can affect the ternary phase diagram, with the PL of a lower molecular weight having a higher solubility in the same MS/water mixture. The presence of free sugar (i.e., levoglucosan, present in bio-oil as solute) also influences the ternary phase diagram of the PL/MS/system, but only at a low water content (i.e., < 20 wt %). The results suggest that such ternary diagrams may be potentially an important tool for predicting the phase separation of bio-oil, as a result of changes in the bio-oil chemistry in various processes (e.g., cold-water precipitation and aging).

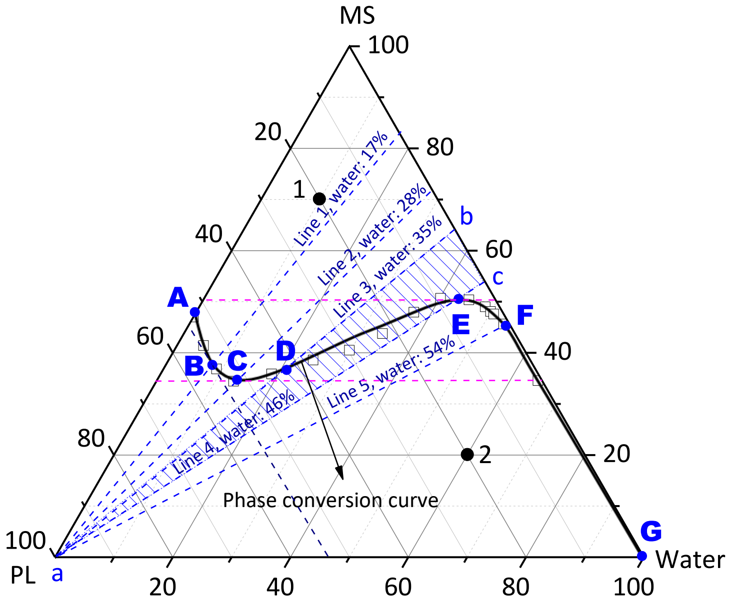

Figure 9 – Ternary phase diagram of the PL/MS/water system

PROPOSAL OF A REPRESENTATIVE CHEMICAL COMPOSITION FOR LIGNOCELLULOSIC PYROLYSIS BIO-OIL AND ESTIMATION OF THE THERMODYNAMIC PROPERTIES OF THE BIO-OIL COMPOUNDS

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Key Words: bio-oil representative composition, thermodynamic properties.

One of the most promising biorefinery platforms is based on the production of bio-oil via fast pyrolysis of lignocellulosic biomass. Lignocellulosic pyrolysis bio-oil is a complex mixture of water and organic compounds coming from the devolatilization and the thermal ejection of the main biomass components (cellulose, hemicellulose, lignin and extractives), but also from secondary reactions of these primary pyrolysis products. The very diverse chemical reactions and phenomena that take place during the pyrolysis process, together with the different structure of biomass constituents, make the pyrolysis bio-oil a mixture of very different compounds, going from light volatile compounds to oligomers and presenting also a wide variety of functional groups. Ultra high resolution mass spectrometry techniques enable the discrimination of thousands of peaks, assigned each one to a unique $C_cH_hN_nO_oS_s$ elemental formula[1]. In the pyrolysis bio-oil biorefinery platform, separation and refining processes are of utmost importance. For this reason, there is an extensive research work on refining treatments of bio-oil[2] and an incipient research work on separation processes[3]. The complexity of the own processes and the multitude of parameters affecting them make their experimental study costly and tedious. The simulation of shortcut refining and separation methods, but also of the own pyrolysis process, could allow assessing the suitability of a certain method or the accomplishment of parametric studies. The availability of a representative chemical composition of the pyrolysis bio-oil and also of the thermodynamic properties of the proposed compounds is a necessary step for the success of any of these simulations. In this context, the two objectives of this work were 1) to propose a simple but representative chemical composition of lignocellulosic pyrolysis bio-oils and 2) to estimate some of the thermodynamic properties of the compounds included in the proposed composition.

Literature[4] and own experimental data have been used to propose the chemical composition. In this way, more than 30 different compounds have been included in the proposed composition, such as, main volatile compounds (e.g. acetic acid, glycoaldehyde, acetol or levoglucosan), some HPLC detectable sugars (galactose or cellobiosan) and three different types of oligomers (pyrolytic lignin, pyrolytic humin and hybrid oligomers). The enthalpy of formation of the non-tabulated compounds included in the composition have been estimated using mainly a group contribution-based method[5]. For the calculation of the enthalpy of formation, it has also been necessary the estimation of other thermodynamic properties, such as the boiling point, the critical pressure and temperature, the enthalpy of vaporization or the Gibbs free energy, among others. Examples of the estimated enthalpies of formation values are: glycoaldehyde $\Delta H^{\circ}_{f,298\ K\ (l)} = -379.9\ kJ\cdot mol^{-1}$, levoglucosan $\Delta H^{\circ}_{f,298\ K\ (l)} = -981.2\ kJ\cdot mol^{-1}$, hybrid oligomers $\Delta H^{\circ}_{f,298\ K\ (g)} = -7774.2\ kJ\cdot mol^{-1}$.

The suitability of the proposed pyrolysis bio-oil composition has been checked using two different ways: 1) the total concentration of some functional groups (carbonyl, carboxyl, hydroxyl, phenolic) determined experimentally by other authors[4] has been compared to their theoretical concentration calculated using the structural formulas of the compounds proposed, and 2) the liquid enthalpy of formation of the pyrolysis bio-oil calculated from the experimental values of heating value and ultimate analysis has been compared to the liquid enthalpy of formation calculated as the weighted average of the estimated enthalpies of formation of the proposed compounds. The differences between the experimental and the estimated values of functional groups concentration and of bio-oil enthalpy of formation were lower than 10%.

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UPGRADING OF WHEAT/BARLEY AND MISCANTHUS BIO-OIL OVER A SULPHIDED CATALYST

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Key Words: bio-oil, hydrogenation, sulphided, catalyst, biofuel

In recent years, the production of biofuels from non-food crops wastes and harvesting residues plays an important role in the improvement of the global environment and in the replacement of declining oil reserves[1]. Hydrogenation of lignocellulosic bio-oil is attracting much attention as a suitable way to produce petroleum-refinery compatible feedstock. Primarily, hydrogenation of bio-oil is carried out under severe reaction conditions in two-stage fixed-bed reactors, filled with a noble metal catalyst in the first zone and with a sulphided catalyst in the second zone[2]. This setup allows producing low-oxygen upgraded bio-oil, however, it is economically unviable and operationally complicated. Here, we present the results from 80 h long hydrogenation experiments of miscanthus and wheat/barley straw bio-oils obtained by one-stage condensation (2-5 °C) or fractional condensation (75 °C) ablative fast pyrolysis (AFP). Bio-oils from fractional condensation, in contrast to those from one-stage condensation, were stable and did not separate into an aqueous and organic phase. In that case, operation with these bio-oils was much easier than with bio-oils from one-stage condensation. Upgrading of bio-oils was performed in a one-stage fixed bed reactor filled with a laboratory-made $NiMo/Al_2O_3$ catalyst under constant reaction conditions (340 °C, 4 MPa and WHSV 1 h^{-1}), which we identified in our previous research as suitable reaction conditions. Hydrogenated products separated spontaneously into an aqueous phase, formed predominantly by water, and an organic phase. In this work, we used various analytical methods for the determination of physicochemical properties (density, viscosity, elemental analysis etc.) and chemical composition (CAN, Carbonyls by Faix, GC-MS for volatile compounds and hydrocarbons) of the organic products. In addition, we used FTIR in combination with the principle component analysis (PCA) to take a snapshot of the catalyst health and product quality. In all hydrogenated products, we have observed a drop in the quality with the increasing time-on-stream, which may be caused by catalyst deactivation and coke formation, as it shown in Figure 2. Nevertheless, the coke formation and reactor clogging, during the hydrogenation of miscanthus bio-oil, was so high that we were forced to stop the experiment after 36 hours. The observed decrease in Micro Conradson Carbon residues and CAN of the products from wheat/barley straw bio-oil indicated a significant improvement of the product stability. The laboratory-made $NiMo/Al_2O_3$ catalyst was suitable for the upgrading of straw bio-oil, from one-stage and from fractional condensation AFP, and can be further developed for the upgrading for other feedstocks.

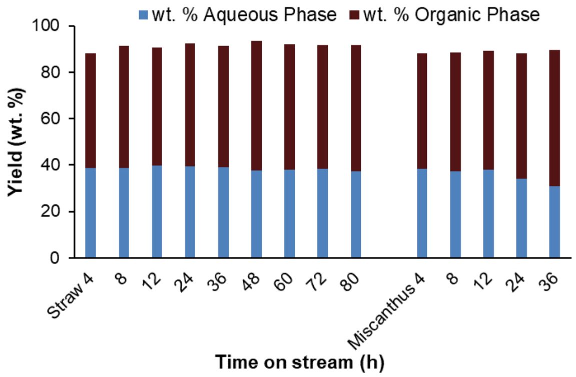

Figure 1 – Yields of aqueous and organic phases from straw and miscanthus bio-oil hydrogenation

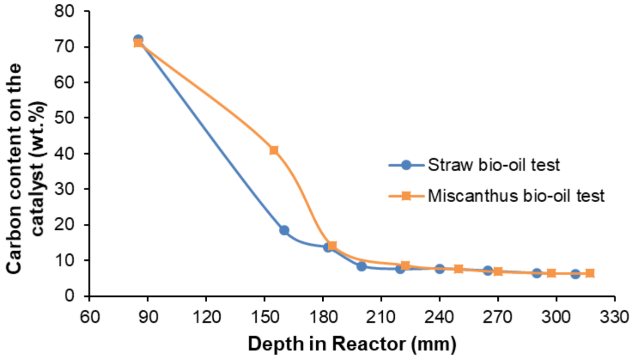

Figure 10 – Carbon content on the catalyst after the experiments

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DEPOLYMERIZATION OF FRACTIONATED WOOD BY HYDROTHERMAL LIQUEFACTION

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Key Words: Biomass, cellulose, fractionation, organosolv, depolymerization, hydrothermal, liquefaction

Direct thermochemical conversion of lignocellulosic biomass produces a mixture of compounds that have to be separated to produce purified building blocks. Moreover, lignin derived products have a detrimental effect on further biological conversion processes, such as fermentation. For all these reasons, it is important to develop an integrated approach for a better fractionation and valorisation of macromolecules (carbohydrates and lignin) in bio-refineries.

In this work, wood is fractionated producing cellulose-rich pulps that are converted by hydrothermal liquefaction into fermentable sugars (*Figure 1*). For this purpose, beech has been delignified either by ethanol organosolv or by sodium chlorite/acetic acid (SC/AA) treatment, obtaining delignification yields of 50 and 91 wt. % respectively. The recovered pulps were then submitted to liquefaction in hot-compressed water (HCW). Three temperatures were studied: 180, 200 and 220°C during 2 h. The same experiments were conducted on untreated beech and model cellulose (Avicel PH-101). Product yields and total carbohydrates were determined. The liquefaction products, i.e. solid residue, water soluble compounds and permanent gas, were analyzed respectively by X-ray diffraction (XRD), high performance anion-exchange chromatography with pulsed amperometric detector (HPAEC-PAD) and gas chromatography (GC). SC/AA treatment allowed a high recovery of hemicelluloses and for this reason, xylose content was significantly higher for the SC/AA pulp. The maximum yields of total carbohydrates, i.e. 13.7 and 36.8 wt.% from the organosolv and SC/AA pulp respectively, were found when the liquefaction temperature was 220°C.

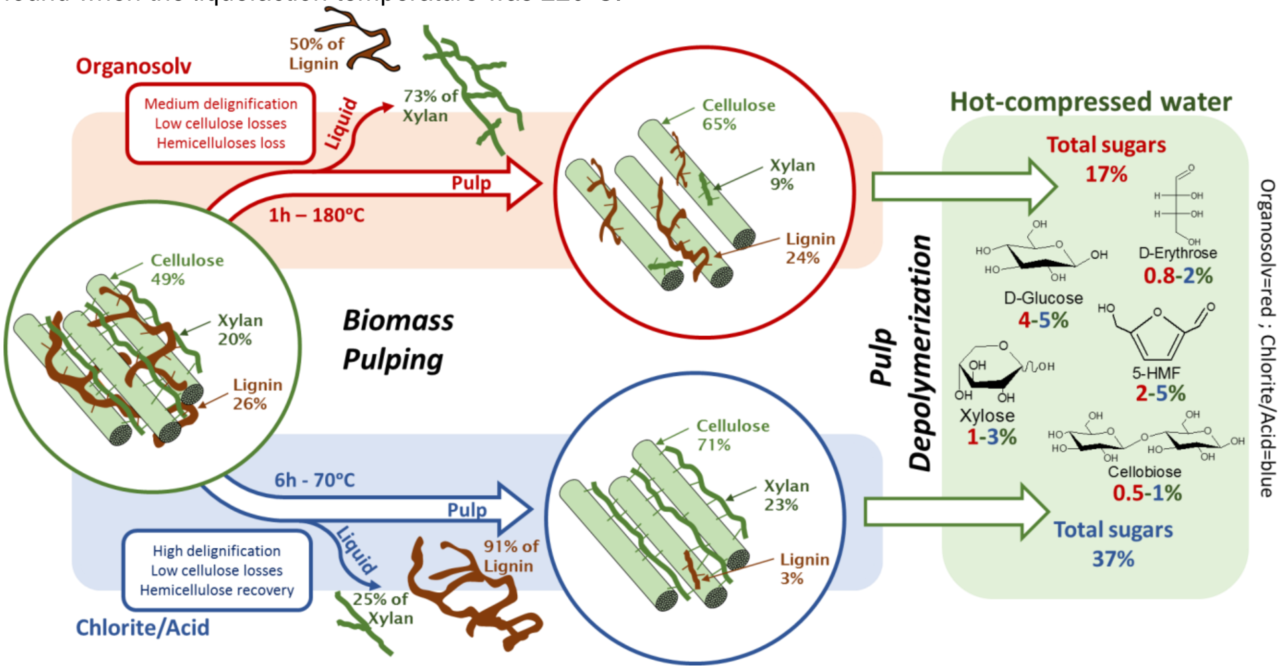

Figure 1 - Schematic representation of the hydrothermal conversion of the wood pulps. Typical yields of the most representatives compounds are indicated.

CHARACTERIZATION OF HYDROPROCESSED FAST PYROLYSIS OIL FRACTIONS

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Key Words: fast pyrolysis, distillation fractions, catalytic upgrading

Production of renewable fuel from biomass has both environmental and national security implications. Considering that liquid transportation fuels massively affects the way we live, technology to produce fuels need to be both technologically-appropriate and economical. Fast pyrolysis remains as one of the most promising thermochemical processing technologies for converting solid biomass into a liquid that can be further upgraded into hydrocarbon fuels. The presence of various types of oxygen-containing functional groups confer pyrolysis oils with unwanted fuel properties such as acidity and low heating value. In order to remove these oxygen functionalities, catalytic hydrodeoxygenation or hydroprocessed is needed. This process involves the catalytic treatment of pyrolysis oils at high temperature and high pressure hydrogen, similar to that employed in the petroleum industry to remove sulfur from crude oil. However, hydroprocessed fast pyrolysis oil is complicated by both the thermal and chemical instability of the pyrolysis oil itself and the presence of water, giving importance to proper catalysts design considerations. Hydroprocessing further produces water and CO_x gas species as a means to expel the oxygen. The aqueous phase typically contains very low to negligible amount of carbon while the organic phase will contain a mixture of hydrocarbons. If the degree of deoxygenation is lower, larger amounts of carbon are present in the aqueous phase while recalcitrant oxygen species, like phenols and carboxylic acids appear in the organic phase. This in turn can affect the composition of the different fractions generated after distillation of the organic phase product.

This presentation aims to discuss both the characterization of the various hydrotreated fast pyrolysis oil fractions, including elemental, ^{13}C NMR and autoignition properties. It will also describe the hydrotreating processes used to obtain the different degrees of deoxygenation.

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ELECTROCHEMICAL UPGRADING OF BIO-OIL: A PROOF-OF-PRINCIPLE INVESTIGATION

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Key Words: biomass, fast pyrolysis, upgrading, electrochemistry, hydrogen.

Fast pyrolysis is an advanced thermochemical conversion technology developed to produce bio-oil from biomass. With lignocellulosic biomass, high product yields (65-75 wt.%) can be attained. Yet, certain unfavorable characteristics of bio-oil impede its utilization prospects. High water content, high oxygen content, together with instability and acidity are the recognized adverse features of bio-oil. Tackling these issues is possible by reducing the oxygen content and/or steering the oxygen functionality of bio-oils.

Electrochemical hydrogenation (ECH) is a recently proposed approach targeting the reduction of the reactive compounds in bio-oil (aldehydes, ketones etc.) to their corresponding alcohols, diols [1]. In this attractive approach, the water present in bio-oil acts as the hydrogen source for reduction reactions. Production of alcohols/diols leads to an upgraded/stabilized bio-oil product. Performing the upgrading at ambient temperature, pressure and providing a means to store intermittently available renewable energy (e.g. solar, wind) are clear advantages of the ECH process.

In this work, we have investigated electrochemical upgrading of bio-oil using water soluble bio-oil (WSBO) as feed. The ECH experiments, carried out in an electrochemical reactor at a current density of 44 mA cm^{-2}, focused on comparison of several cathode materials. Separated by a cation exchange membrane, cathode and anode chambers of the reactor were filled with WSBO (ca. 20 wt.% bio-oil in aqueous solution) and 1M H_2SO_4, respectively. The tested cathode materials included Ti, Ru-coated Ti (Ru), Pt-coated Ti (Pt), stainless steel (SS) and CuZn (brass) electrodes. All electrodes converted the carbonyl groups present in bio-oil to a certain extent following the order CuZn>>SS>Ti>Pt>Ru. The trend is explained in close relation with the hydrogen evolution reaction, the preferred pathway especially with Pt and Ru electrodes. Despite the high conversions achieved for some compounds, the selectivity towards desired alcohols and diols was not very high (e.g. 15 – 49% ethylene glycol selectivity for glycolaldehyde conversion) for the electrodes tested in this study. Low Faradaic efficiencies obtained are considered as another challenge keeping the conversion costs high.
Nevertheless, electrochemical hydrogenation appears to be a promising technology to upgrade/stabilize bio-oil that deserves further investigation. Next to the experimental results obtained, possible future improvements in catalytic cathode selection and processing options will be discussed as well.

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CHALLENGES AND OPPORTUNITIES FOR THE SYNTHESIS OF NOVEL PYROLYSIS OIL REFINERIES

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Key Words: Pyrolysis oil, bio-oil, bio-refining, co-products

Bio-oil derived from fast pyrolysis of lingo-cellulosic materials is among the most complex and inexpensive raw oils that can be produced today. Although commercial or demonstration scale fast pyrolysis units can readily produce this oil, this industry has not grown to significant commercial impact due to the lack of bio-oil market pull. In this presentation we will review the challenges and opportunities for bio-oil upgrading and refining. Pyrolysis oil consists of six major fractions. (water 15-30 wt.%, light oxygenates, 8-26 wt. %, mono-phenols, 2-7 wt.%, water insoluble oligomers derived from lignin 15-25wt.%, and water soluble heavy molecules 10-30 wt.%). The composition of water soluble oligomers is relatively poorly studied. In the 1880s bio-oil refining (formally known as wood distillation) targeted the separation and commercialization of C1-C4 light oxygenated compounds to produce methanol, acetic acid and acetone with the commercialization of the lignin derived water insoluble fraction for preserving wooden sailing vessels against rot. More recently Ensyn extracted and commercialized condensed natural smoke as a food additive. Most research efforts in the last twenty years have focused on the two-step hydrotreatment concept for the production of transportation fuels. In spite of major progress this concept remains at the demonstration scale. In this presentation, the opportunities and progress to separate bio-oil fractions and chemicals, mainly acetic acid (HAc), hydroxyacetaldehyde (HHA) and acetol, and convert them into value added co-products are thoroughly discussed. In spite of the large number of separation schemes and products tested, very few of them have been studied as part of fully integrated bio-oil refinery concepts. During our presentation we will discuss the synthesis, techno-economic and environmental evaluation of novel integrated bio-oil refinery concepts.

COST ESTIMATION OF A BIOREFINING NETWORK FOR FOREST RESIDUES IN IRELAND

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Key Words: Cost Estimation, Multi-criteria Decision Analysis, GIS, Pyrolysis, Hydrothermal Liquefaction

The forestry sector in the Republic of Ireland (ROI) is mainly focused on harvesting timber from the stems of spruce trees. The remaining 30-35% of unharvested wood volume, typically known as forest residues or brash, is left on the forest floor. Only a small geographically specific portion of forest residues are bundled and sold at low cost as fuel for industrial combined heat and power (CHP). The volume of unused forest residues in ROI is estimated to be 700 thousand $m^3\,a^{-1}$, and its distribution is shown in Figure 1[1]. This significant quantity can be mobilized as biomass feedstock to biorefineries for high value bio-products. The composition, quantity and type of feedstock available in Ireland indicate that pyrolysis and hydrothermal liquefaction (HTL) are the most effective biorefining pathways. Bio-oils produced from pyrolysis have high energy value and HTL uses forest residues with high moisture content as feedstock saving the cost of drying. Both of these technologies have the capability to be energy neutral and therefore have potential at the small, distributed scale found in Ireland [2]. The highly dispersed nature of forest residues coupled with low energy density presents challenges in sustaining substantial availability of feedstock to the biorefinery. Selection of an optimum location for building a biorefinery can help design an efficient supply chain to reduce transportation cost and environmental impact. Multi-criteria decision analysis (MCDA) coupled with geographic information system (GIS) analysis is a popular and effective method to analyse location suitability. Localised criteria can either be factors, which influence location suitability, or constraints, which limit development in that vicinity. These criteria are weighted using the analytical hierarchy process (AHP) and combined in GIS to give a final site suitability map. Selection of the most cost-effective location out of all suitable sites requires a cost estimation model that will compare the operational cost for both technologies and transportation cost of the resources and final product.

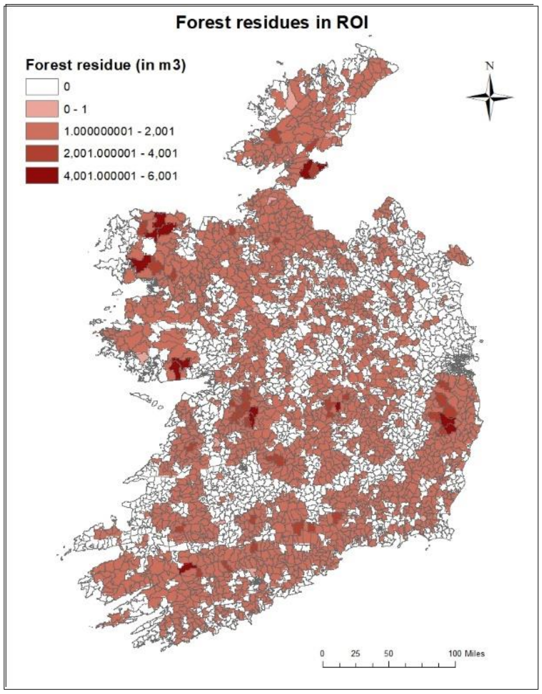

Figure 11 – Forest residue distribution in ROI

This work will (1) present a decision support tool (DST) for siting a biorefining infrastructure in Ireland, (2) assess the economic aspects of pyrolysis and HTL for conversion of forest residues in Ireland, and (3) develop a cost estimation model to determine the most cost-effective site. The DST is map-based and employs MCDA using ArcGIS software, which involves defining, evaluating and weighting economic and environmental criteria, followed by a sensitivity analysis. The cost estimation model will be based on step cost method. The site with the lowest operational and transportation costs will be selected as the location for building the biorefinery. The results of the present work will be used to conduct life cycle assessments of specific high-potential bio-products in future work.

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ENVIRONMENTAL ASSESSMENT OF PYROLYSIS IN BIOREFINERIES BASED ON PALM OIL WASTES

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Key Words: Palm Oil, Pyrolysis, Energetic Analysis, Life Cycle Assessment

The oil palm industry is one of the largest producers of residual biomass, leading to environmental and economic concerns. For this reason, the concept of biorefinery is emerging as a means to create new ways of converting biomass into new types of renewable products bioenergetics that can contribute to the reduction of greenhouse gases. In this context, this document presents a study that consisting of a biorefinery configuration in a Palm Oil Mill (POM), considering the fast pyrolysis process to produce bio-oil and biochar, and an extraction / trans-esterification stage to produce biodiesel and glycerin in the POM. The environmental impacts associated with a production process of a biorefinery system were calculated using the life cycle assessment methodology through the IMPACT 2002+ method, which analyzes the environmental impacts in four categories of damage (human health, ecosystem quality, climate change and resources). Therefore, to produce bio-oil, biodiesel and electricity were obtained 52 mPt, 120 mPt and 127 mPt of total impacts, respectively, demonstrating that the fast pyrolysis process to obtain bio-oil it does not generate considerably high environmental impacts compared with the other products obtained in the biorefinery in any of the categories of damage assessed.

INFLUENCE OF REACTOR TYPE ON PRODUCTION COST OF FAST PYROLYSIS BIO-OIL

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Key Words: Fast Pyrolysis, Biomass Residues, Reactor, Process Design,

The design of a fast pyrolysis reactor to convert biomass has a decisive influence on quality and yield of fast pyrolysis bio-oil (FPBO). Quality requirements are comparably low for the application of FPBO as gasifier fuel for subsequent conversion to synthesis gas, e.g. in the case of the bioliq® concept to convert (ash-rich) agricultural residues to drop-in, 2nd generation biofuels. Within this concept, one optimization parameter of fast pyrolysis is to maximize carbon yield in the liquid product while keeping product requirements that allow feeding into a high-pressurized entrained flow gasifier. This optimization space allows for a more flexible choice of reactor design. The aim of this study is to investigate the influence of reactor type on production cost of FPBO within above outlined framework, i.e. as feedstock for a downstream gasifier.

The investigation will be based on two different type of reactors. First, a twin-screw mixing reactor (TSMR) is being considered, which resembles the actual realization of the 500 kg h^{-1} fast pyrolysis pilot unit that is being operated as part of the bioliq® project. Second, a fluidized bed reactor (FBR) will be compared to that, which represents state of the art technology of industrial fast pyrolysis units. One important difference between the two reactors is the necessity of a fluidizing agent in case of the FBR, which in turn influences process design and equipment size, specifically in the product recovery section. This additional (inert gas) volume flow is not required in the case of a mechanical mixing, as is the case in the chosen TSMR. At the same time it is obvious that there will be a significant difference in mixing conditions of biomass and heat carrier particles in the two types of reactors, which will translate to a difference in heating rate of the biomass particles. This in turn might affect FPBO quality and yield.

Experiments have been conducted to compare FPBO yields from process development units that feature a TSMR and an FBR, respectively. No significant differences in FPBO yield have been observed. On the one hand this leads to the conclusion that the high heat transfer required to achieve one of the fast pyrolysis conditions (i.e. high temperature of primary pyrolysis inside the biomass particle) is comparable in both types of reactors. This could be explained by the high bulk density achieved during mechanical agitation as compared to that of a fluidized bed, which is capable of making up the lower mixing intensity if a proper ratio of biomass to heat carrier particles is kept. On the other hand, wheat straw (which is the 'model' feedstock for the bioliq® project) was used as feedstock in these experiments This choice might also lead to not observing differences between the two reactor types. Wheat straw is characterized by high ash content (around 8%) which increases the significance of secondary cracking reactions and thus lowers any effects of reactor type. Wheat straw also exhibits high heterogeneity which translates to increased standard deviation of the results (confirmed by multiple test runs) and an increased difficulty to detect differences in FPBO yield.

Based on the experimental results, the effect of process design on FPBO production cost are reduced to investment and operation cost. Existing production cost calculations for the bioliq® concept have been reviewed and updated due to the currentness of the underlying data. Additionally, relevant process design changes and equipment cost will be implemented for consideration of an FBR instead of the TSMR. Finally, a sensitivity analysis is conducted to reflect changes in product yield based on available literature data for fast pyrolysis of wheat straw in order to account for the previously discussed uncertainty of the obtained experimental results.

PYROLYSIS OF AEROBIC SEWAGE SLUDGE, GREEN WASTES AND REFUSE DERIVED FUELS AT HIGH TEMPERATURES IN BUBBLING FLUIDIZED BED REACTOR

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Key Words: Pyrolysis, wastes, syngas, fluidized bed.

Effect of temperature during Flash Pyrolysis of solid wastes (Green wastes -GW-, sewage sludge -SS- and refuse-derived fuels -RDF-) in inert atmosphere was investigated in the present study. Pyrolysis was carried out in a dense fluidized bed reactor of laboratory scale (2.5 m height, 0.214 m inner diameter) where wastes are fed continuously. Experiments were conducted at temperatures between 700 and 900°C with different types of fluidized media to highlight the effect of these parameters as well as the influence of the waste nature on gas production rate and carbon distribution into pyrolysis products. For instance, the syngas produced during sewage sludge pyrolysis is rich with H_2, CO, CO_2, CH_4 and C_2H_X. For SS thermal decomposition, The increase of temperature from 700 to 890°C enhances the syngas production yield from 0.22 to 0.90 $Nm^3/kg\ daf_{,B}$ and reduce the tar yield from 388.55 to 131.69 g/kg of waste $daf_{,B}$. According to these results, we proposed a pyrolysis diagram at different temperatures by estimating stoichiometric coefficients related to incondensable gas, char, tars, water and micropollutants.

<u>Thermal decomposition diagram of aerobic sewage sludge at high temperatures:</u>

$$CH_{1.67}O_{0.32}N_{0.08}S_{0.008} + 0.1051H_2O \Rightarrow \alpha_{H2}H_2 + \alpha_{CO}CO + \alpha_{CO2}CO_2 + \alpha_{CH4}CH_4 + \alpha_{C2H4}C_2H_4 + \alpha_{C2H6}C_2H_6 + \alpha_{C2H2}C_2H_2 + \alpha_{char}CH_{0.06}N_{0.005} + \alpha_{NH3}NH_3 + \alpha_{HCN}HCN + \alpha_{N2}N_2 + \alpha_{H2S}H_2S + \alpha_{C6H6O}C_6H_6O + \alpha_{C6H6}C_6H_6 + \alpha_{C7H8}C_7H_8 + \alpha_{C10H8}C_{10}H_8 + \alpha_{H2O}H_2O.$$

Table 12 – Pyrolysis diagram of aerobic sewage sludge at temperature between 700 and 890°C in sand fluidized bed; measured coefficients.

Temperature (°C)	H_2	CO	CO_2	CH_4	C_2H_4	C_2H_6	C_2H_2	Char
700	0,0467	0,0470	0,0281	0,0275	0,0281	0,0030	0,0002	0,2600
750	0,1170	0,1008	0,0676	0,0657	0,0613	0,0000	0,0007	0,2200
800	0,1196	0,1034	0,0570	0,0924	0,0700	0,0013	0,0011	0,2000
830	0,1423	0,1280	0,0523	0,0701	0,0648	0,0024	0,0018	0,2000
850	0,1592	0,1388	0,0599	0,0978	0,0720	0,0028	0,0011	0,2000
870	0,2135	0,1763	0,0687	0,1211	0,0806	0,0038	0,0014	0,2000
890	0,2746	0,2235	0,0508	0,1299	0,0693	0,0038	0,0007	0,2000

Table 2 – Pyrolysis diagram of aerobic sewage sludge at temperature between 700 and 890°C in sand fluidized bed; estimated coefficients.

Temperature (°C)	NH_3	HCN	N_2	H_2S	Phenol	Benzene	Toluene	Naphthalene	H_2O
700	0,0787	0,0000	0,0000	0,0080	0,0225	0,0346	0,0208	0,0087	0,2995
750	0,0789	0,0000	0,0000	0,0080	0,0087	0,0306	0,0150	0,0081	0,1803
800	0,0495	0,0147	0,0074	0,0080	0,0046	0,0327	0,0120	0,0080	0,2032
830	0,0750	0,0022	0,0009	0,0080	0,0031	0,0391	0,0110	0,0079	0,1893
850	0,0536	0,0149	0,0052	0,0080	0,0015	0,0365	0,0061	0,0066	0,1651
870	0,0376	0,0256	0,0079	0,0080	0,0000	0,0281	0,0036	0,0043	0,1113
890	0,0129	0,0435	0,0113	0,0080	0,0000	0,0250	0,0025	0,0037	0,1000

SLOW PYROLYSIS OF LIGNIN RICH RESIDUE FROM LIGNOCELLULOSIC BIOREFINING OPERATIONS

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Key Words: lignin, slow pyrolysis, torrefaction, biorefinery residues, char.

Europe is committed to have a bio-based economy in 2030. It follows that a huge contribution of biorefinery products on the European demand for chemicals, energy, materials and fibers is expected in the near future. To be environmentally and economically sustainable, biorefinery will need to be flexible, versatile, energy and cost efficient [1]. In a lignocellulose based biorefinery, the sugar platform that leads to bioethanol and added-value products through biochemical processes represents a challenging option. After ethanol distillation a lignin reach residue (LRR) is produced and used as energy source. However, it is currently underutilized with about 60% more lignin generated than is needed to meet the internal energy use [2, 3]. The exploitation of this residue for the combined production of biofuels and added value chemicals and materials represents a key factor for the increase of the efficiency of the overall ethanol production chain and its valorization is mandatory for the viability of future biorefinery operations.

Biomass pyrolysis is a very flexible thermochemical treatment that in the absence of molecular oxygen is capable of producing a solid residue (char) suitable for application in several fields and liquid (bio-oil) and gaseous products that can be exploited for energy production or as chemicals' source. By properly tuning the main process variables (temperature, heating rate, carrier gas flow rate) the pyrolysis process can be guided towards the maximization of the yields and/or the optimization of the quality of the desired products. To this aim a comprehensive knowledge of the thermal behavior of the biomass is needed. A lot is known about pyrolysis of many types of lignocellulosic biomasses and of cellulose, one of the main biomass organic components However, lignin was less explored and even less the LRR from ethanol production that is contaminated by micro-organisms and not-hydrolyzed sugars [4].

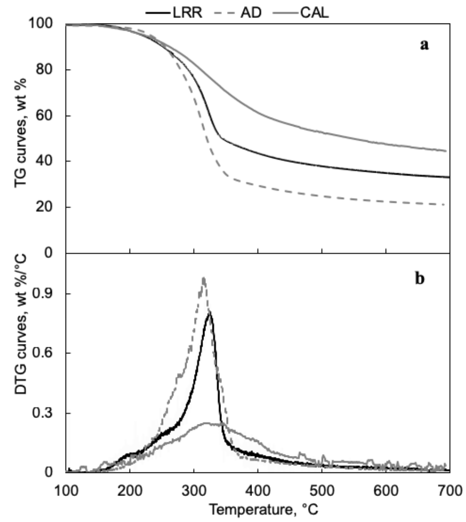

Figure 13 – TG (a) and DTG (b) curves of LRR, commercial alkali lignin (CAL)[5], and arundo donax (AD)[6] obtained at 10 °C/min.

In this work a preliminary study on the thermal behavior of the LRR under nitrogen atmosphere was conducted. Thermogravimetric analysis (cf. Fig. 1) and pyrolysis tests were performed at 10 °C/min exploring a wide range of final temperatures from 300 to 700 °C. The pyrolysis products yields (gas, liquid and char) and the composition of the gas mixture were quantified and the evolution of the gaseous products during the process was monitored. Chemical and physical analyses were carried out on the chars in order to investigate changes in the elemental composition, volatile matter content and porosity characteristics as a function of the temperature.

The char yields, the elemental composition and the porosity characteristics allowed to deduce that LLR had a thermal behavior very different from the alkali lignin typically used as reference compound for biomass lignin. Both products yields and char composition were more similar to the typical values of woody and herbaceous biomasses. The chemical characterization of the chars' organic matrix as well as the content of the main inorganic species suggest the possibility to perform pyrolysis at low temperature for producing high yields of chars suitable to be used as carbon sink or soil fertilizers. The BET values of chars obtained at final temperature in the range 500 -700 °C seem to be promising for char application in processes involving surface phenomena (e.g. adsorption, catalyst support), thus encouraging further analyses on porosity characteristics and surface chemistry.

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THE APPLICATION OF PYROLYSIS BIOCHAR FOR WASTEWATER TREATMENT

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Key Words: Pyrolysis; Biochar; Oxidation; Cation exchange; Lead

Pyrolysis as a common method of biocrude oil and biochar productions, is the thermal conversion of biomass under limited concentration of oxygen. Biochar, the solid product of pyrolysis process, is largely used in the applications connected with surface density of acidic functional groups (FGs) and biochar specific surface area (SSA), such as adsorption, catalysis, and soil amendment. In this work, the application of pyrolysis biochar in the adsorption of lead cations from aqueous solutions was investigated. Biochar was provided by Pyrovac Inc. (Québec, Canada) from shredded wood comprising 20% volume of spruce/fir and 80% pine (stem of Pinus strobus without bark). The pyrolysis was performed at 475°C for 1 h under atmospheric pressure, resulting in a biochar yield of 27.8% on a feedstock anhydrous basis.

Our results showed that, as expected, untreated biochar has a very low tendency to adsorb lead cations, owing to the low surface density of oxygen-containing FGs. In order to increase the cation exchange capacity (Q) of the biochar, mild air oxidation was implemented under the following conditions: $m_{char} = 2$ g, $T = 200°C$, $t = 60$ min, $Q_{air} = 165 \pm 10$ cm^3 min^{-1}. Mild air oxidation then increased the total concentration of acidic surface FGs from 2.2 to 6.8 mmol g^{-1}, which was quantified using Boehm titration. This improvement upon the simple mild air oxidation, thus, increased the biochar adsorption capacity of Pb^{2+} under equilibrium adsorption conditions of $m_{char} = 0.5$ g per 50 cm^3, $C_{Pb}{}^{2+} = 1000$ ppm, pH = 5, and t = 48 h, from 2.5 to 44 mg g^{-1}. These results are comparable with those of biochar chemically modified by using acids, bases, and salts such as H_2SO_4, KOH, and $KMnO_4$, as reported in literature[1–3].

The external surface of biochar was investigated by XPS and SEM/TEM analyses. The deconvolution of C_{1s} XPS photo-line showed that the most significant increase in the XPS peak area upon oxidation was obtained for the one attributed to carboxylic FGs, from 1.7 to 8.2%. Comparing XPS peak areas of oxidized biochar before and after the equilibrium adsorption, suggested that carbonyl and carboxylic FGs on the outer surface of oxidized biochar, as well as aromatic rings, participated in Pb^{2+} removal. SEM showed that biochar surface was loaded with lead cations, heterogeneously, especially at the edge of particles surface ducts.

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HYDROTHERMAL CONVERSION OF MICRO-ALGAE AS NEW BIOMATERIALS FOR PAVEMENT

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Key Words : Hydrothermal liquefaction, microalgae residues, rheological properties, bioasphalt

Bitumen is a non-renewable petroleum-derived product whose market is under pressure due to the fossil fuel depletion and the environmental pollution concerns. It is therefore important to anticipate the replacement of this material, heavy fraction of petroleum distillation, used mostly in road construction as a matrix of an aggregate composite material. In that context, it is necessary to look for alternatives or substitution products and find processes that can valorize new renewable biomasses.

Scenedesmus and Spirulina residues, coming from a first industrial valorization, have been identified as a potential biomass for this application as well as hydrothermal liquefaction (HTL), which is a promising organic solvent-free thermochemical process able to convert those residues into a viscous liquid fraction.

For each microalgae residue, an hydrophobic material was recovered after HTL. This bio-crude has been characterized by different analytical techniques (GCxGC-MS, NMR, GPC, FT-IR, elemental analysis…). Then, the rheological behavior of those oils was measured and compared to a petroleum bitumen. One residue showed a rheological behavior similar to a petroleum-based bitumen while the other microalgae residue presented a viscoelastic behavior similar to a bio-sourced binder loaded with a high percentage of elastomers. We studied as well the influence of the HTL conditions (addition of a catalyst, temperature, reactor loading…) on the bio-crude chemical composition and rheological behavior.

Figure 14 – Hydrothermal liquefaction of microalgae residues into bioasphalt

POLYMER FROM PYROLYSIS PRODUCTS

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Key Words: Pyrolysis, Bio-oil, Microwave, Liquid system, Polymer

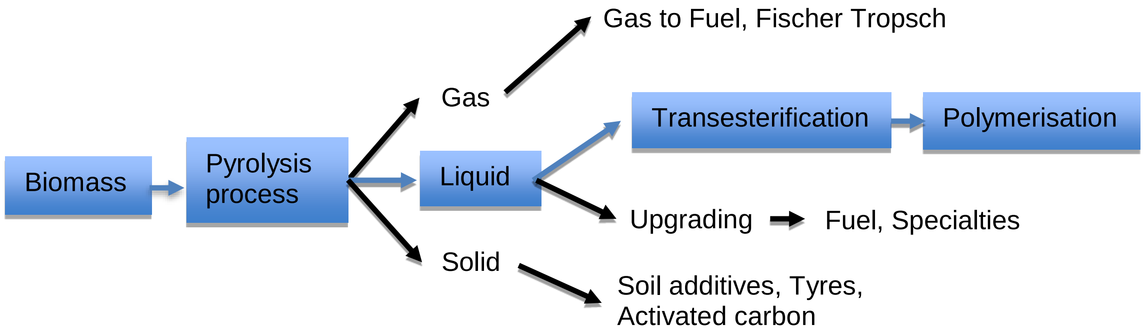

Figure 15 Potential routes to value from pyrolysis products, with the focus of this project, “pyrolysis products to polymer”, shown in blue.

Polymers are used every day; they are an indispensable part of our lives. If we want to maintain our plastic dependant lifestyles and expand our population alternative feedstocks for polymers need to be found. Pyrolysis is a possible route to useful materials however it is difficult to control and analyse the composition of liquid[1] and produce economically viable product[2].Microwave pyrolysis involves lower temperature during pyrolysis and can give more controlled products compared with the conventional method[3]. It is anticipated to produce multiple pyrolysis liquids that are potentially input materials for a variety of processes. The focus of this work will be the synthesis of polymers from pyrolysis liquids and how pyrolysis liquid composition affects the behaviour of the product. This work could see a new family of polymers with properties dependant on the composition of pyrolysis liquid. This could help to reduce the use of crude oil for polymers.

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EVALUATION OF THE ANTIFUNGAL ACTIVITY OF CATTLE MANURE BIO-OIL

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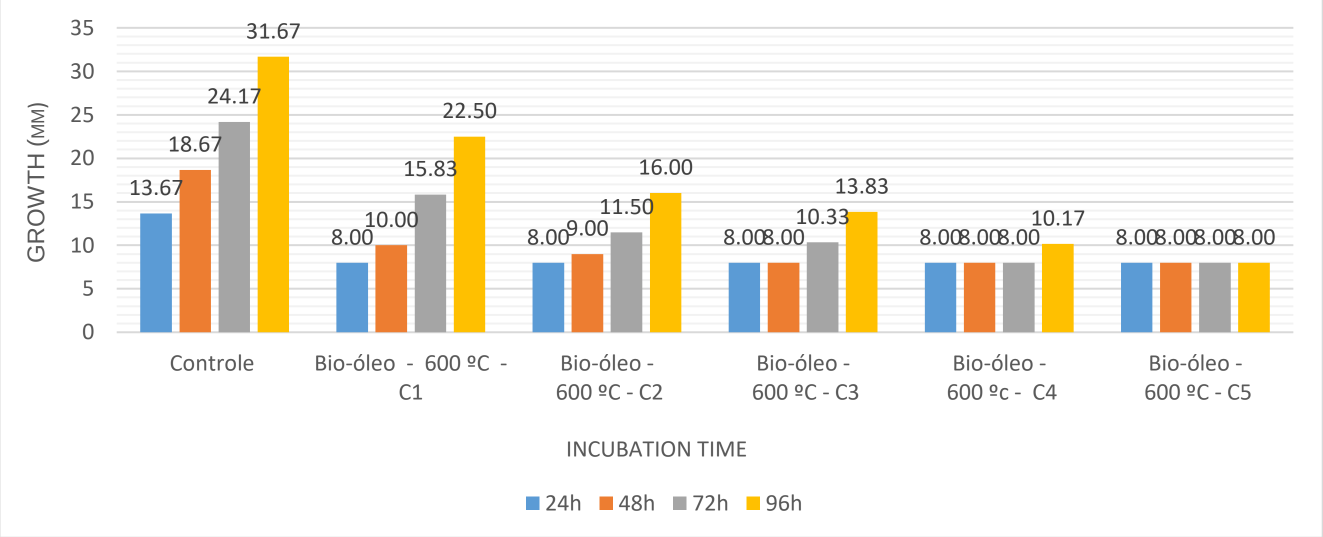
Key Words: Bio-oil, pyrolysis, alternative fungicides, phytopathogenic fungi, cattle manure.

Plant diseases are a threat to the health and functionality of both natural and man-made ecosystems. Diverse methods and strategies are being employed to prevent, ameliorate or control plant diseases. Unsustainable practices such as use and misuse of synthetic fungicides have caused severe harm to human health, wildlife and the environment (1). Fungal cause the most destructive plant diseases and impose major losses to both natural and production systems, and one of it is the fungi. Botanical fungicides are particularly sought after because they are abundant, selective, readily degraded, and are not toxic to mammals (2).

Bio-oils produced by rotatory kiln pyrolysis reactor at 400 °C, 500 °C and 600 °C had their antifungal activities tested by the disc-diffusion technique. The bio-oil samples were used at concentrations of 1000 µg mL^{-1} (C1), 2000 µg mL^{-1} (C2), 3000 µg mL^{-1} (C3), 4000 µg mL^{-1} (C4) and 5000 µg mL^{-1} (C5) against two types of phytopathogenic fungi, *Fusarium solani* and *Lasiodiplodia theobromae*, saprophytic species capable of living in the soil for long periods that devastate the production of citrus fruits. Furthermore, DMSO (dimethylsulfoxide) was used as the surfactant with concentration of 1% in the samples.

In general, cattle manure bio-oils presented satisfactory fungistatic potentials, reaching higher than 50% of growth inhibition, and the one produced at 600 °C presented the best result, achieving 95% inhibition of growth against the fungus of the genus *Lasiodiplodia*. Against *Fusarium*, the bio-oil produced at the highest temperature was able to inhibit 100% of its growth at the same concentration C5. The samples were characterized using GC/MS and a predominance of phenolic compounds was observed, among them phenol, which had a concentration of 12.35% in the samples. Therefore, it is suggested that this antifungal action is correlated to the predominant presence of phenolic compounds in the sample, which act by penetrating the fungal cytoplasmic membrane, altering its selective permeability, vital for the maintenance of vital intracellular substances.



Graph 1 - Growth in mm of the fungus Fusarium solani in the presence of the bio-oil produced at 600 °C.

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HYDROTHERMAL RECYCLING OF ACTIVATED BIOCHAR

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Key Words: Activated biochar, Emerging pollutants, Hydrothermal treatment, Wastewater treatment

Emerging pollutants such as pharmaceuticals are of increasing concern in wastewaters. Carbon materials such as activated carbons prove to be effective filter materials for the removal of these pollutants, but regeneration of the adsorbents is necessary to improve their economic efficiency. However, common thermal regeneration methods using dry adsorbents and high treatment temperatures are expensive and hinder large scale applications in wastewater treatment plants [1]. Novel adsorbents such as biochars are seen as an alternative due to their lower production costs [2]. However, considering their generally lower adsorption capacity, costly regeneration will abolish the initial economic advantage of biochar. In contrast to fully regenerating the original adsorptive properties, we argue that a recycling step to prepare biochar for different subsequent applications can produce a higher value product. In this study we propose a method using hydrothermal treatment to decontaminate activated biochars. Two standard biochars from the UK Biochar Research Centre produced at 550°C from softwood and wheat straw were activated in CO_2 at 800°C. Additionally, the same raw feedstocks were mixed with 5% Ochre, pyrolyzed and activated at the same conditions to produce two activated mineral biochar composites. The biochars were loaded with 10 pharmaceuticals commonly found in wastewaters and decontaminated in a hydrothermal reactor at temperatures ranging from 160 to 320°C for 4 hours at autogenic pressure. To avoid catalytic effects from the reactor walls, a novel experimental design based on standard borosilicate test tubes was developed. The sample is placed into a test tube, filled with water, flame sealed and placed into a hydrothermal reactor. The outer reactor is filled to the same level as the sample tube to counterpressure the glass and avoid bursting during the experiment. With this set-up, an inert and disposable reactor liner ensures comparable reaction conditions between runs and eliminates potential cross contamination. After the hydrothermal treatment, the biochars as well as the process water were analyzed by LC-MS/MS for remaining pharmaceuticals. Hydrothermal treatment was found to fully degrade 8 out of 10 investigated pharmaceuticals at a treatment temperature of 200°C, with almost complete degradation of the remaining pharmaceuticals at 320°C. The results show that hydrothermal treatment has the potential to recycle activated biochar and enable its use in subsequent applications such as gas filtration systems for the removal of H_2S or as an additive for increased gas production in anaerobic digestion plants.

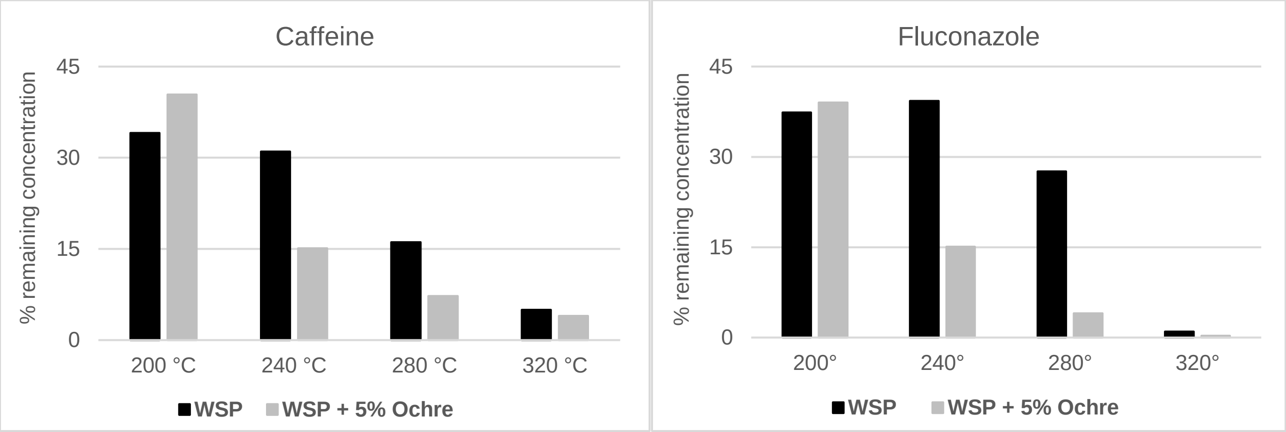

Figure 16 & 2: Concentration of the 2 detectable pharmaceuticals after hydrothermal treatment. WSP – activated wheat straw biochar, WSP + 5% Ochre – mineral biochar composite containing 5 % Ochre.

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ANAEROBIC DIGESTION OF THE AQUEOUS PYROLYSIS CONDENSATE

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Key Words: Aqueous pyrolysis condensate, anaerobic digestion, pyrolysis, biochar, methane

Fractional condensation of biomass pyrolysis vapors allows the segregation of different pyrolysis fractions and a separation of an aqueous pyrolysis condensate from an organic rich dry bio-oil fraction. Aqueous pyrolysis condensate is often referred at as “wood vinegar” or “pyroligneous acid” since it contains 70-80% water together with 10-20% acetic acid, and smaller quantities of acetone and methanol mixed with hundreds of other chemicals in small concentrations. Such aqueous pyrolysis condensate cannot be easily disposed of, and it may represent a valuable resource. For example, the significant percentage of acetic acid offers the opportunity to attempt its conversion into methane by anaerobic digestion.

Aqueous pyrolysis condensate produced by fractional condensation of vapors generated from the pyrolysis of birch bark at 500 °C has been characterized (elemental composition, pH, COD, volatile fatty acids (particularly acetic acid), ammonia, hydrogen sulfide, minerals, and phenolics), inoculated with a consortium of bacteria from an organic waste anaerobic digestor, and digested over several weeks. Biogas production has been progressively monitored and methane and CO_2 concentrations experimentally measured.

We performed a large number of experiments to investigate the effects of (a) dilution of the aqueous pyrolysis condensate, (b) nutrients addition, and (c) addition of bio-char on the production of biogas and on its methane concentration.

The results clearly show that the anaerobic digestion of aqueous pyrolysis condensate is possible and leads to the production of biogas and on the reduction of the COD of the original feedstock to make it suitable for disposal. However, the high phenolic content of the condensate, together with possibly other chemical species, creates considerable inhibition of microbial methane production. Such inhibitory effects, however, can be mitigated by gradual adaptation of the bacteria population to the feedstock composition. The result show that 50 to 60 days are required before significant biogas production is observed when raw anaerobic pyrolysis condensate is processed. The addition of bio-char to the process is beneficial in shortening the lag phase to approximately 20 days and is triggering a higher volume of biogas production with an increased methane content, compared to similar conditions without bio-char. This is attributed to the ability of bio-char to adsorb inhibitory compounds as well as to create more favorable environmental conditions for the digestion process. Similarly, but less effectively, the addition of selected nutrients is shown to benefit the anaerobic process by shortening the lag phase to 40 days.