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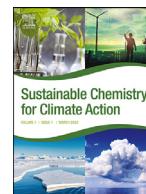
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The synthesis of biooil using ambient pressure liquefaction of organic waste

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ABSTRACT

To realize a sustainable alternative to fossil fuels, carbon neutral sources such as biowaste should be converted to biooil. This paper reports the results of our study on the catalytic liquefaction of various organic waste (mandarin peel, coffee grounds and cocoa shell) to synthesize an oil which can be used as a sustainable fuel. Out of the tested reactions, spent coffee ground liquefaction proved to yield the best results when catalyzed by phosphotungstic acid (PTA). Increasing the catalyst loading resulted in an increasing yield, with the maximum yield of 40 % obtained with a catalyst loading of 38 wt%. The resulting oil contained compounds mainly in the desired C8-16 range (79 %) that is required for jet fuel. While most of these compounds were oxygenated compounds an upgrading reaction should allow the oil to be used as a sustainable jet fuel alternative.

1. Introduction

Fossil fuels are non-renewable energy sources that contribute greatly to the high emission of greenhouse gases in modern world [1]. To reduce the harmful effect imposed by fossil fuels, an increasing amount of research is conducted into the creation of more sustainable alternatives to fossil fuels [2–6]. Unfortunately fossil fuels are still employed massively due to economic reasons such as the presence of a large amount of industrial infrastructure dedicated to fossil fuel manufacturing and overall cheaper relative production costs [7,8]. However nowadays governments all over the world are realizing the negative impact of fossil fuels and are encouraging and subsidizing to replace these with the more sustainable alternatives [9]. For cars dependence on fossil fuels can easily be replaced with the introduction of the electric car. Improving these electric cars and fueling them with sustainably obtained electricity will be the most promising green future of road transportation [7]. This is however not possible for the aviation industry. Due to long flight times and high speeds, the power needed is too high to produce for an electric motor [10]. Thus, to increase the sustainability of the aviation industry a green alternative to jet fuels is necessary. A promising method to produce bio jet fuels is by using biomass as renewable feedstock. Biomass is a renewable carbon source because it directly absorbs CO₂, making the production of fuels out of biomass a carbon neutral process [10]. A multitude of bio-jet fuels have already been produced and some are even already employed by commercial airlines.

Compared to regular petrol used in cars the fuels used in jet engines are held to higher standards [11]. The common properties attributed to effective jet fuels are: hydrocarbons in the range of 8-16 carbon atoms, a low freezing point and kinematic viscosity and a high gravimetric net

heat of combustion (NHOC). To be able to implement the sustainable jet fuel in actual aerial transportation, the bio fuels should also meet these properties. To obtain these properties, bio-oil should be upgraded, if necessary, to yield a fuel that can be used in existing engine systems or as blendstock in combination with existing fuels [10]. A plethora of techniques have been used to convert biomass into bio-oils, of which a commonly employed technique is biomass liquefaction.

Liquefaction is a technique that converts solid biomass (which mainly consists of lignin, cellulose and hemicellulose) into a liquid bio-oil [1,12]. This reaction breaks the big polymeric compounds in biomass into smaller monomers, which can subsequently react further to obtain the final compounds present in the bio-oil. The complex bio-oil mixture consists of numerous compounds, including: alkanes, aromatic hydrocarbons, phenol derivatives, ketones, esters, ethers, sugars, amines, and alcohols [1,12]. The compounds formed depend on the composition of the used biomass, as all these substances have different degradation behaviors [13]. The range of the formed monomers are usually between 5-20 carbon atoms long, with lignin rich compounds centering around C11 compounds, while cellulose is more inclined towards C8 and C10 products. Therefore liquefaction is a suitable technique to obtain oil capable of functioning as jet fuel. As well as creating the desired range of small molecules, the liquefaction procedure also increases the quality of the oil (C/H ratio) [14].

To increase the efficiency of the liquefaction, a catalyst can be employed [15]. Research has proven that (Bronsted)-acid catalysts are the most useful catalysts for biomass liquefaction. They increase the efficiency of the reaction and lower the required reaction temperature [6,15–18]. Most research employs liquid acids in order to facilitate the liquefaction, however this acid will need to be neutralized after the

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reaction is done. This neutralization adds additional steps and reagents to the process, hindering its economical and industrial viability by increasing production costs. The use of liquid acids is also disadvantageous because of the inherent danger of working with low pH liquids due to their corrosive nature which can lead to damage to personnel or equipment. To circumvent these downsides a solid acid catalyst can be employed. Employing solid acids for biomass liquefaction also have some additional benefits such as an easier separation from the bio-oil and the possibility to recycle the catalyst. Some solid acid catalysts have been shown to exhibit superior yields in cellulose rich biomass compared to liquid acids [18]. However the poor solid-solid interaction between a solid acid catalyst and biomass is problematic for the reaction system [19].

A promising solid acid candidate is phosphotungstic acid (PTA), which is a Keggin-type heteropoly acid (HPA) and has already been employed in a multitude of green reactions, including liquefaction [19–23]. HPA's are often classified as solid super acids due to their high acidity [24]. The high acidity of HPAs makes them good catalysts for liquefaction, of which the efficiency relies heavily on the strength of the used acid. Some benefits of employing HPA's include low toxicity, environmental friendliness and commercial availability, but the main benefit of employing HPAs such as PTA for the liquefaction of biomass is their ability to dissolve in polar solvents such as water and alcohol [19]. Solvation of the catalyst eliminates the poor solid-solid interaction that hampers other solid acid catalysts in liquefaction. A promising polar solvent that has already been employed in combination with an acid catalyst in liquefaction is ethylene glycol (EG) [25]. This green solvent can be made from biomass, is widely available and the polar groups allow for solvation of PTA [26].

A few studies were already carried out for the liquefaction of biomass. Tylisha et al. [27] were able to use hydrothermal liquefaction in supercritical water to convert micro algae into bio-oil with a yield of 43 wt%. Wang et al. [28] were able to liquefy sawdust in ethanol, using K_2CO_3 at 300 °C to yield 30.8 wt% oil. Kohansal et al. [29] also used a homogeneous K_2CO_3 catalyst and succeeded in liquefying municipal solid waste into a bio-oil (yield 36.6%) at a temperature of 350 °C. This yield was increased to 49.3% by utilizing recirculation of the aqueous phase. By using waste as a source of 2nd generation biomass for the liquefaction, a more sustainable bio-oil can be created than when 1st generation biomass is employed, for it ensures that the synthesis of bio-fuel doesn't compete with the production of food [6]. Thus, research into conversion of bio waste into high quality fuel is an area of biomass liquefaction that has a promising future for the synthesis of sustainable bio jet fuels. This was also acknowledged by Katakojwala et al. [30] who used hydrothermal liquefaction without catalysts and at high temperature (350 °C) and H_2 pressures (100 bar) to convert municipal waste into a green bio-oil (yield 18%). Wang et al. [17] used kitchen waste as biomass and obtained a higher yield of 52.4%, using acidic additives, proving that the presence of acid enhances the liquefaction.

The use of acid catalyst, biowaste, green solvents, low temperature and pressure are all critical factors in the synthesis of a more sustainable bio-oil. The objective of this paper is to study the conversion of different organic waste into bio-oil using a liquefaction that employs a solid acid catalyst and EG. The end goal is to get a bio-oil that attains the properties required for easy upgrading into jet fuel.

2. Experimental

2.1. Materials

The chloroform and 1,4-dioxane were both 99.9% solvent grade purity and obtained from Biosolv, the phosphoric acid (85%) was bought from Alfa Aesar, phosphotungstic acid, sodium hydroxide pellets and ethylene glycol were bought from Merck chemicals. The organic waste (mandarin peel and spent coffee grounds) used as feedstock was regular kitchen waste from products obtained from the supermarket. They

were pretreated by drying at 110 °C for 12 hours, afterwards they were blended to a rough powder and used in the experiments. Pre dried cocoa shell was supplied by Olam. The cocoa shell flakes were ground up into a fine powder before use in the reaction.

The sulfonated ZnO-TiO₂ catalyst ($SO_4^{2-}/ZnO-TiO_2$) was made using the following method published by Zhu et al. [31]: A solution of 0.2 M $Ti(SO_4)_2$ and 0.2 M $Zn(Ac)_2$ was prepared. Aqueous ammonia (25%) was added into the solution dropwise while the solution was strongly stirred at 20 °C until pH reached 8. The stirred solution containing the precipitate was kept in an oil bath for 4 h at 70 °C. This solution was filtered and washed with distilled water and dried for 16 h at 120 °C. Afterwards, the powder was ground and subsequently impregnated with 0.5 M $(NH_4)_2SO_4$ solution (15 ml/g) at 20 °C under constant stirring for 4 h followed by drying at 120 °C for 16 h. Finally the powder was calcined for 3 h at 300 °C and 500 °C respectively.

2.2. Liquefaction using a liquid acid catalyst

Biomass feedstock (2 g) and 85% H_3PO_4 (0.745 ml, 14.4 mmol, 1eq) were added to ethylene glycol (20 ml). The mixture was refluxed at 180 °C for 4 h, afterwards the flask was allowed to cool for 16 hours. To this 1,4-dioxane (80 ml), which is recommended as a general solvent for liquefied biomass was added and the solids were filtered out [32]. The solid fraction was dried at 105 °C for 12 h and weighed. The resulting liquid fraction was neutralized with 0.1 M aqueous NaOH (~80 ml) and concentrated in vacuo. This was then placed in a separatory funnel and water (40 ml) was added to create a two phase system. The organic layer was washed with chloroform (3 × 100 ml) and collected. The organic layer was concentrated in vacuo (the chloroform that evaporated could be recycled). The resulting oily product was weighed and characterized.

The bio – oil yield was calculated as : $Y_{Biooil}(wt\%) = \frac{W_{biooil}}{W_{biomass}} \times 100\%$

The biomass conversion was calculated as :

$$X_{Biomass}(wt\%) = \frac{W_{solid\ residue} - W_{solid\ catalyst}}{W_{biomass}} \times 100\%$$

2.3. Liquefaction using a solid acid catalyst

Biomass (2 g) and the desired solid catalyst (37.5 wt%) were added to ethylene glycol (20 ml). The mixture was refluxed at 180 °C for 4 h, afterwards the flask was allowed to cool for 16 hours. To this 1,4-dioxane (80 ml) was added and the solids were filtered out (Fig. 1) [32]. The solid fraction was dried at 105 °C for 12 h and weighed. The resulting liquid fraction was reduced in vacuo and placed in a separatory funnel. Water (40 ml) was added to create a two phase system and the organic layer was extracted with chloroform (3 × 100 ml) and collected. The organic layer was concentrated in vacuo (the chloroform that evaporated could be sublimated and recycled). The resulting oily product was weighed and characterized (Fig. 2).

The PTA catalyst was recycled by submerging the 1,4-dioxane insoluble solid residue in water (80ml) and stirring for 30 minutes. The insoluble residue was filtered out while the water was evaporated for 16 hours at 110 °C.

2.4. Product characterization

For the GC analysis the samples were prepared by dissolving the oil (1 ml) in acetonitrile (1ml). These samples were analyzed by using a gas chromatograph (PerkinElmer Clarus 580) equipped with a HP-5 column (30 m x 0.32 mm x 0.25 μm). The used program was as follows: temperature 60 °C (hold for 5 min) → 280 °C (25 °C/min, hold for 3 min); 0.5 μl of sample was injected and the detector temperature was 320 °C.

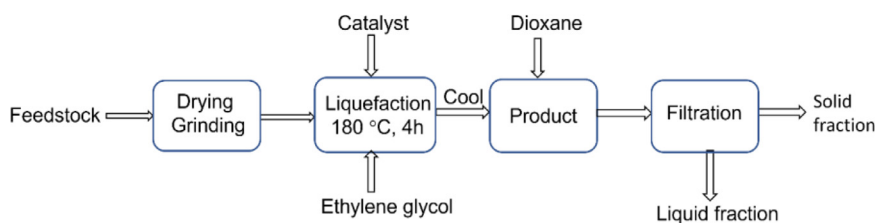


Fig. 1. A simple schematic showing the reaction procedure.

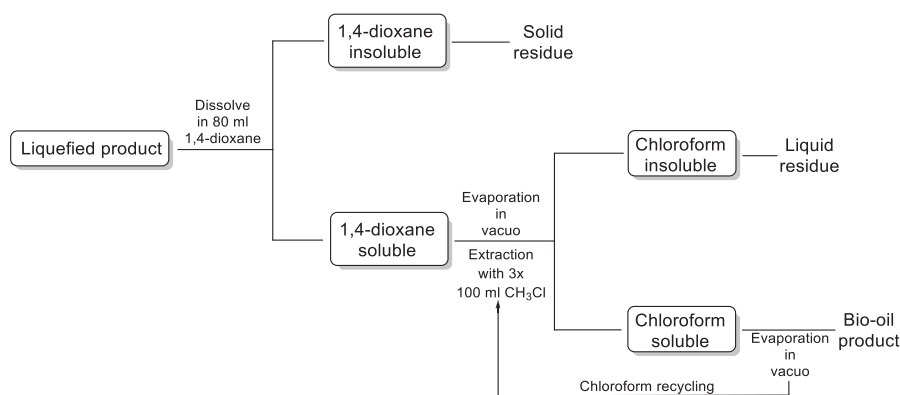


Fig. 2. The separation procedure of the liquefied biomass.

For the GC-MS analysis, the samples were prepared by dissolving the oil (10 μ l) in chloroform (1ml). These samples were analyzed by using a gas chromatograph (Shimadzu GC-2010) coupled to a mass spectrometer (Shimadzu GCMS-QP2010), equipped with a DB-5 column (30 m x 25 mm x 0.25 μ m). The used program was as follows: temperature 70 $^{\circ}$ C (hold for 5 min) \rightarrow 180 $^{\circ}$ C (8 $^{\circ}$ C /min, hold for 5 min) \rightarrow 320 $^{\circ}$ C (10 $^{\circ}$ C /min, hold for 5 min), 1 μ l of sample was injected at 305 $^{\circ}$ C, detector working at 320 $^{\circ}$ C, a linear velocity of 40 cm/s and a split of 100. After a 3 min solvent delay, full-scan mass spectra were acquired from 50 to 500 m/z. The spectra were interpreted using an NIST automatic database.

3. Results and discussion

3.1. Conversion and yields of the biomass liquefaction

According to the literature the yield and quality of the bio-oil depends on the reaction conditions, catalyst used and type of biomass [11]. We used different catalysts and organic waste to find an optimal combination for an efficient biomass liquefaction, while the other reaction conditions such as temperature (180 $^{\circ}$ C), pressure (1 atm) and reaction time (4h) were kept constant. In this paper 3 different biomasses were considered: mandarin peel, spent coffee grounds and cocoa shell. The cocoa shell functions as a more rigid lignin rich biomass, while the mandarin peel and coffee grounds are typical examples of common kitchen waste. For the catalyst 3 types were tested: a liquid acid (H_3PO_4), solid heteropoly acid (PTA) and solid acid ($\text{SO}_4^{2-}/\text{ZnO-TiO}_2$). The yields and conversions for the tested feedstock and catalyst combinations are reported in Fig. 3. The first observation is that not all of the biomass conversion results in bio-oil. This is due to the fact that next to liquid oils also gaseous and solid products are formed [13]. These gasses mainly consist of CO, CO_2 and methane. The solid residue is usually in the form of carbon, which is filtered out in the first separation step. All these byproducts are removed during the separation process and don't contribute to the final bio-oil yield.

A relatively high conversion is obtained for mandarin peel. This however does not translate into a high bio-oil yield, the contrary is actually observed as it showcases the lowest bio-oil yield of all tested feedstocks. The reason could be the increased formation of non-liquid products when mandarin peel is liquefied under these reaction conditions. Espe-

cially the formation of more gaseous products is the main contributor to this observation.

Cocoa shell has the lowest overall conversion with comparable results between all catalysts. The low conversion is likely a result of the high lignin content present in cocoa shells, which is harder to convert into a bio-oil and usually results in the formation of more solid residue [6]. When the yield is examined a peculiar trend is discovered. The liquid H_3PO_4 catalyst shows the lowest bio-oil yield, followed by the PTA, then the $\text{SO}_4^{2-}/\text{ZnO-TiO}_2$, also note that the bio-oil yield is the highest for the cocoa shell liquefaction that employed no catalyst. Since conversions are comparable the catalyst probably has no effect on the liquefaction as a whole, but the distribution in the three types of products (solids, liquids and gasses) is in fact affected. The liquefaction without a catalyst shows the baseline bio-oil yield of 30 %, with the rest of the conversion into gas or solids. When an acid catalyst is added, which is proven to usually improve the liquefaction, the yield of the organic oil fraction decreases while retaining comparable biomass conversion. This implies that either more gaseous products are formed or other byproducts that don't dissolve in the chloroform fraction of which the final oil is extracted. This leads to the hypothesis that the use of a (strong) acid catalyst catalyzes the reaction towards the unwanted byproducts, instead of the wanted bio-oil. Thus liquefaction of the more lignin rich cocoa shells with an acid catalyst under these reaction conditions is not effective if the aim is the production of a high quality oil. However a bio-oil yield of 30 % is notable for a reaction without catalyst. Katakajwala et al. [30] were able to get up to 18 % with a reaction without catalyst, while employing higher pressures (100 bar H_2) and temperatures (350 $^{\circ}$ C).

The most promising results were obtained when coffee grounds were employed as feedstock. The catalytic liquefaction performed significantly better than the non-catalytic counterpart, with the highest yield (40 %) being obtained by the solid PTA catalyst. This is greater than a previous liquefaction performed by Wang et al. [28] for the direct liquefaction of sawdust in ethanol who were able to reach a yield of 31 wt%. This yield is also comparable to the 43 wt% yield obtained by Tylisha et al. [27] by hydrothermal liquefaction of micro algae in supercritical water. However the liquefaction in this paper used a more widely available biomass and used a lower temperature and pressure. But the main benefit of this reaction is that it doesn't utilize a supercritical solvent in order to reach this yield. Supercritical solvents and

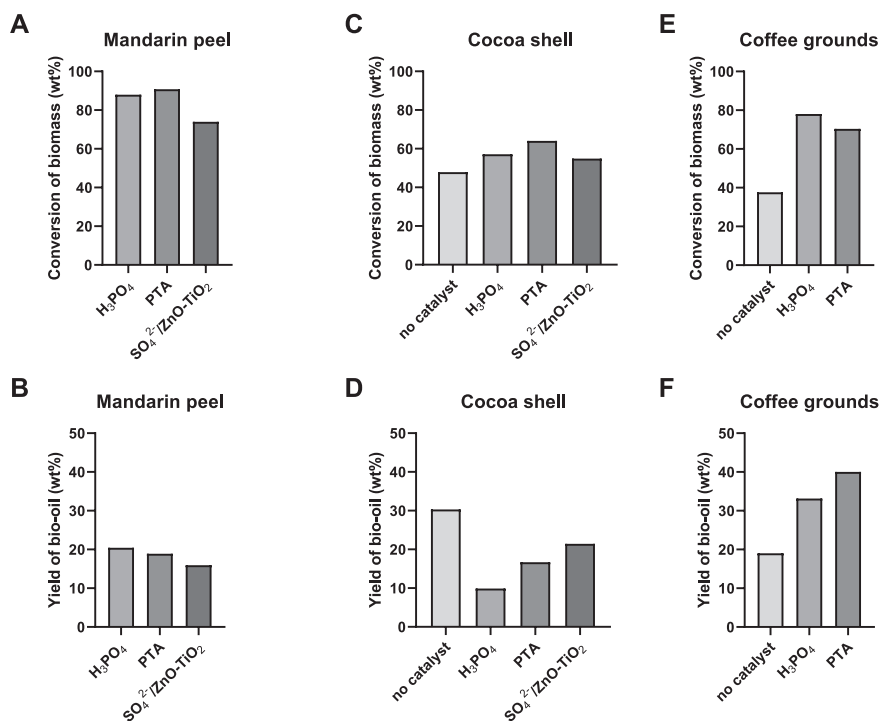


Fig. 3. Biomass conversion and bio-oil yield of various biomasses using different catalysts. Reaction conditions: 180 °C, 4 h, solvent: ethylene glycol (20 ml), biomass (2 g), catalyst (38 wt%). A and B show the conversion of mandarin peel and yield of bio-oil from mandarin peel respectively. C and D show the conversion of cocoa shell and yield of bio-oil from cocoa shell respectively. E and F show the conversion of coffee grounds and yield of bio-oil from coffee grounds respectively. The conversion of mandarin peel was about 30% without any catalyst.

higher pressures and temperatures increase the operating costs for industrial processes, thus the coffee ground liquefaction is able to scale up to industrial standards more easily. In the coffee ground liquefaction the solid PTA catalyst even outperforms the liquid phosphoric acid catalyst, allowing for a combination of the more favorable properties of a solid acid (less corrosive, no need for a neutralization step and catalyst recyclability) with a competitive yield.

Finally we will take a look at the sulfonated ZnO-TiO₂, this catalyst did not have any outstanding results for any of the tested biomass. This was likely due to the poor solid-solid interaction between the catalyst and the solid biomass [19]. As a result the big polymers were unable to interact with the active sites of the catalyst and thus they were unable to be broken into smaller compounds which are present in the liquid bio-oil. The only reaction where the SO₄²⁻/ZnO-TiO₂ outperformed the other catalysts was when cocoa shells were used as biomass. But as mentioned before this is likely due to the fact that the other catalysts catalyzed the reaction path towards the gaseous products, which the SO₄²⁻/ZnO-TiO₂ catalyzed to a lower degree, leading to a higher relative liquid bio-oil yield. As the SO₄²⁻/ZnO-TiO₂ catalyzed cocoa shell reaction attained a lower yield than the non-catalytic counterpart, the use of this catalyst has no major advantage.

3.2. Effects of PTA catalyst loading and recycling for coffee grounds liquefaction

Out of all tested reactions the PTA catalyzed coffee ground liquefaction showcased the most promising results, for it has high bio-oil yield and moderately high conversion. In order to improve the effectiveness of this reaction the effects of the catalyst loading as well as the catalyst recycling has been studied (Fig. 4).

Both conversion and yield increase with a higher catalyst loading, indicating that a higher catalyst loading has a positive effect on the liquefaction (Fig. 4). When a low amount of PTA is employed, the yield was below 20%, however when loading was 38 wt%, high yield of 40% is obtained for the biooil. Since the highest tested catalyst loading is 38 wt%, the trend suggests that increasing the catalyst loading might result in an even higher biomass conversion and bio-oil yield. However, employing large amounts of catalyst in a reaction also lead to an increase in cost for the final bio-oil. To obtain the optimal catalyst loading for

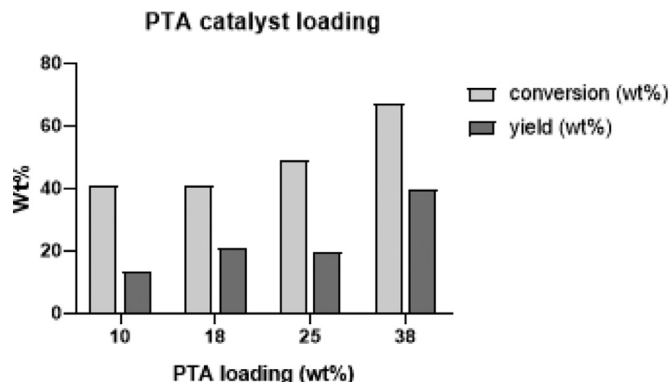


Fig. 4. Bio-oil yield and conversions of coffee ground liquefaction using different PTA loading. Reaction conditions: 180 °C, 4 h, solvent: ethylene glycol (20 ml), coffee grounds (2 g).

a large scale industrial liquefaction of coffee grounds using PTA, an in depth cost analysis should be conducted that weighs the increased yield against the cost of a higher catalyst loading.

The cost of a high catalyst loading can be counteracted if the used catalyst is recovered and reused for multiple reaction cycles. The recycling of the PTA catalyst was attempted by submerging the solid residue of the liquefaction (which contains the unreacted biomass and the PTA catalyst) in water. The polarity of water should allow the PTA to dissolve, while the unreacted biomass remains a solid to be easily filtered out. Most of the catalyst could be recovered by this method and reused. The recovered catalyst gave similar levels of activity in the subsequent liquefaction.

3.3. Analysis of the bio-oil

To determine the composition of the bio-oil, we did the analysis of the bio-oil by GC and GC-MS. The initial GC analysis reveals that the used catalyst has no impact on the amount of compounds that are present in the bio-oil. However the used biomass does influence on the composition of the created oil. The coffee ground liquefaction yielded

Table 1

GC-MS analysis of the bio-oil obtained from different C-containing feedstocks. Reaction conditions: 180 °C, 4 h, solvent: ethylene glycol (20 ml), biomass (2 g), PTA (38 wt%).

Peak number	Retention time (min)	Area (%)	Formula	Compound
Mandarin peel				
1	11.0	2.5	C ₅ H ₁₀ O ₂	2,2-Dimethyl-1,3-dioxolane
2	11.6	31.4	C ₉ H ₁₆ O ₂	2(3H)-Furanone, 5-(acetyloxy)dihydro-5-methyl
3	14.5	3.2	C ₈ H ₁₂ O ₂	4,5-Dimethylcyclohexane-1,3-dione
4	14.9	58.0	C ₉ H ₁₆ O ₄	1,3-Dioxolane-2-propanoic acid, 2-methyl-, ethyl ester
5	29.6	3.0	C ₁₈ H ₃₆ O ₃	2-Hydroxyoctadecanoic acid
Cocoa shell				
1	11.0	4.8	C ₅ H ₁₀ O ₂	2,2-Dimethyl-1,3-dioxolane
2	14.6	5.9	C ₇ H ₁₄ O ₂	2-Butyl-1,3-dioxolane
3	14.8	4.1	C ₉ H ₁₆ O ₄	1,3-Dioxolane-2-propanoic acid, 2-methyl-, ethyl ester
4	15.4	4.3	C ₁₅ H ₂₄ O	2,6-Di-tert-butyl-4-methylphenol
5	20.4	12.9	C ₈ H ₁₀ N ₄ O ₂	1,7-Dimethyl-3,7-dihydro-1H-purine-2,6-dione
6	21.2	59.0	C ₈ H ₁₀ N ₄ O ₂	3,7-Dimethyl-3,7-dihydro-1H-purine-2,6-dione
7	28.4	3.5	C ₁₈ H ₃₆ O ₃	2-Hydroxyoctadecanoic acid
8	30.4	4.0	C ₁₈ H ₃₄ O ₃	Ricinoleic acid
9	30.6	1.6	C ₂₀ H ₄₀ O ₃	2-Hydroxyeicosanoic acid
Coffee grounds				
1	3.9	11.0	C ₄ H ₁₀ O ₃	2,2'-Oxybis(ethan-1-ol)
2	10.3	6.6	C ₆ H ₁₄ O	2-Methoxy-2-methylbutane
3	11.1	5.2	C ₅ H ₁₀ O ₂	2,2-Dimethyl-1,3-dioxolane
4	11.7	15.3	C ₉ H ₁₆ O ₂	2(3H)-Furanone, 5-(acetyloxy)dihydro-5-methyl-
5	15.0	38.2	C ₉ H ₁₆ O ₄	Ethyl 3-(2-methyl-1,3-dioxolan-2-yl)propanoate
6	16.2	4.6	C ₉ H ₁₀ O ₂	5-Isobutylidihydrofuran-2(3H)-one
7	17.8	1.7	C ₁₁ H ₂₀ O ₃	Ethyl (1-hydroxy-2,2-dimethylcyclopentyl)acetate
8	19.1	9.6	C ₁₁ H ₂₀ O ₄	Ethyl 3-(2-propyl-1,3-dioxolan-2-yl)propanoate
9	20.4	2.78	C ₈ H ₁₀ N ₄ O ₂	Caffeine
10	28.4	2.2	C ₁₈ H ₃₆ O ₃	2-Hydroxyoctadecanoic acid
11	30.3	2.5	C ₁₈ H ₃₄ O ₃	Ricinoleic acid

the oil with the most variety of different compounds, followed by mandarin peel and finally the cocoa shell liquefaction had the least. In order to obtain more information about the nature of these compounds a GC-MS analysis was conducted, of which the results are shown in Table 1.

The compounds that are most beneficial for jet fuel purposes are hydrocarbons in the C8-16 range. The analysis of the GC-MS spectra of the PTA catalyzed biomass liquefaction indicates that the amount of compounds in this range is 93 %, 80 % and 79 %, for mandarin peel, cocoa shell and coffee grounds respectively. The mandarin peel oil lacks the large acids that are present in cocoa shells and coffee grounds oil, which are outside the desired carbon range.

Cocoa shell liquefaction (Table 1) created an oil with 80 % of the compounds in the C8-16 range, however the majority of these are nitrogen bearing pyridine derivatives (72 %). These nitrogen bearing compounds are detrimental to fuel properties for they cause corrosion, gum formation and metal complexation [33]. If this oil is to be used for jet fuel all of these pyridine derivatives need to be removed through a denitrogenation step. This will unfortunately add another step to the industrial process, resulting in higher production costs. If these nitrogen bearing compounds are removed however very little actual usable oil will be left (9 %). The liquefaction of cocoa shell is thus not an effective reaction if jet fuel synthesis is required. However, for the synthesis of pyridine derivatives, cocoa shell liquefaction might prove a promising candidate.

The oil from the coffee grounds (Table 1) also shows a small amount of a nitrogen bearing compounds in the form of caffeine. Fortunately the low amount that is present (3 %) does not deteriorate the fuel properties significantly, has little influence of the final yield and can be removed by denitrogenation. The relatively high amount in the desired carbon range (79 %) in combination with the high bio-oil yield (40 %) make the PTA catalyzed coffee ground liquefaction a promising method. However, the bio-oil has high oxygen content. Oxygenated compounds are disadvantageous for fuels because they cause high viscosity, low volatility, corrosiveness, and thermal instability [34]. However, the oxygen can be

removed using various oil upgrading techniques like hydrodeoxygenation (HDO), adding an additional step to the process but increasing the value and C/H ratio of the fuel considerably. This reaction allows the removal of oxygen and has already been commercialized, allowing for easy industrial implementation [12,35–37]. An alternative approach is to use this oil as a blend stock in combination with fossil fuels to combine the sustainability of the bio-oil with the superior properties of the fossil fuel [8]. The liquefaction reaction outlined in this paper is suitable for up-scaling as it involves common unit operations and feasible reaction conditions.

4. Conclusion

The liquefaction of various C-containing feedstocks with a range of acid catalysts in ethylene glycol provided biooil containing different compounds. Highest conversion was obtained with mandarin peel, but the bio-oil yield was the lowest among feedstocks studied. The cocoa shells showed similar results to mandarin peel, but with a slightly higher yield. Among the reactions we studied, spent coffee ground liquefaction yielded the best results when catalyzed by PTA. Increasing the catalyst loading increased the yield, giving a biooil yield of 40 wt % with a catalyst loading of 38 wt %. This solid heteropoly acid catalyst gave the highest yield, even higher than the commonly used liquid acid (H₃PO₄). The use of a solid acid instead of a liquid acid forgoes the need for a neutralization step in the procedure, thus improving industrial viability. GC-MS analysis showed that most of the compounds present in this oil are in the C8-16 range (79 %), which makes it a prime candidate for the production of jet fuel. However most of these compounds are oxygenated and thus further bio-oil upgrading should be performed before this oil can be used as a sustainable jet fuel.

With the increase in use of the resources for our various needs, the waste will only increase in the future. For example, almost 1 billion tons of food ends up as waste each year globally [38]. This contaminates the land as well as water resources, increasing the biochemical

oxygen demand (BOD), and promoting the growth of harmful organisms. Similarly, there is a significant increase in agricultural waste worldwide. Also, residues generated during the harvest are significant. There are several such organic waste streams that need proper handling. Approaches such as outlined in this paper need to be developed further to tackle this major societal problem.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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