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Experimental studies of hydrothermal liquefaction of kitchen waste with H^+, OH^- and Fe^{3+} additives for bio-oil upgrading

Lixian Wang[1], Yong Chi[1], Di Shu[1], Elsa Weiss-Hortala[2], Ange Nzihou[2] and Sangmin Choi[1]

Abstract

Kitchen waste (KW) has gradually become a prominent problem in municipal solid waste treatment. Hydrothermal liquefaction (HTL) is a promising method used to make fuel oil from food and KW. However, the upgrading of bio-oil is particularly important for the sake of industrial reuse. In this study, the KW from university restaurants was subjected to HTL experiments in order to study theoretical feasibility. With the change of conversion temperature and residence time, the optimal conversion working conditions in this study were determined according to the quality and yield of the bio-oil. Moreover, the bio-oil upgrading effects of different additives (hydrogen chloride, sodium hydroxide, and iron(III) chloride) on the HTL of KW were studied. Alkaline additives have an inhibitory effect on the bio-oil yield and positive effect on coke yield. Acidic additives and iron (Fe)-containing additives can promote bio-oil yield. As an important aspect of upgrading, the effect on the nitrogen content of bio-oil with additives was revealed. The alkaline and Fe-containing additives have little effect on reducing the viscosity of the bio-oil while with the appropriate ratio (2.5 mol•kg^{-1}) of acidic additives to the raw material, the static and dynamic fluidity of the oil phase products are reduced to about 0.1 Pa•s.

Keywords

Hydrothermal liquefaction, kitchen waste, bio-oil upgrading, element distribution, molecular properties, viscosity

Introduction

According to statistics of the Food and Agriculture Organization of the United Nations, around one-third of the annual food produced in the world for human consumption gets lost or wasted resulting in a large amount of municipal solid waste (MSW) (Food and Agriculture Organization of the United Nations, 2017). More than half of Chinese MSW is kitchen waste (KW) (Chen et al., 2010), organic waste produced by households and restaurant kitchens (Yuan et al., 2019). In the People's Republic of China (PRC), the increase of KW is putting tremendous pressure on the environment (Ding et al., 2017). In many developing countries (e.g., PRC), MSW generally has a high water content resulting from the relatively high proportion of KW (He et al., 2013). In Malaysia, MSW contains more than 70% of KWs and the landfill system is the main waste management option for MSW in Malaysia (Hafid et al., 2017). In the United States, more than one-third of all food produced is wasted every year, with the majority of it ending up in landfill (Gunders and Blooom, 2017). There is also a similar situation in New Zealand where organic waste including KW is the largest amount of waste deposited in a landfill, counting for 28% (Saqib et al., 2019). Facing a serious problem of over 120 million tons of KW by 2020 in Europe, anaerobic digestion (AD) has become an important part of the circular economy package and is the main food waste treatment method (Zhou et al., 2020). AD is a common biotechnology for converting organic waste into energy (Bong et al., 2018). But significant compositional variations of spices in KW make AD of KW for biogas production a worldwide challenge (Sahu et al., 2017). Moreover, AD can also lead to some soil structure and fertility problems (Maroušek et al., 2020). Composting shows an effective work to utilize the KW because of its high organic content (Abdullah and Chin, 2010). However, by-products, such as leachate and malodour, from the

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imbalanced nutrients are discharged, causing secondary environmental pollution, especially in areas with high population density (Zhang et al., 2016). Due to an immature market, there are still social and economic problems (Maroušek et al., 2015). Although rich content of protein in KW makes it a material for preparing animal feed by feeding treatment (Loizidou et al., 2017), some prevention and control measures should be taken to avoid serious animal epidemics caused by animal protein feed (Li et al., 2016). Direct burning of KW is not a good option because of the aggregation of nitrogen (N) and chlorine in biomass (Mardoyan and Braun, 2015).

Hydrothermal processes of biomass conversion attract growing attention because of several potential advantages in energy recovery, waste reduction and production of high added-value materials (Gallifuoco et al., 2018). Hydrothermal liquefaction (HTL) is a thermochemical process in which organic materials are converted into bio-oil under subcritical water conditions at 280–370°C and between 10 and 25 MPa (megapascals) (Behrendt et al., 2008; Déniel et al., 2016a). The main products are bio-oil with a relatively high heating value, coke, water-soluble substances and gas (Toor et al., 2011). As the most potent technology in breaking the biomass macromolecules into fragments (Kim and Um, 2020), HTL avoids the energy input for drying biomass required by traditional thermochemical conversion processes such as rapid pyrolysis (Xu and Savage, 2017). The bio-oil from HTL of biomass is suitable for upgrading to liquid fuel (Xiu and Shahbazi, 2012). The comprehensive analysis shows that the bio-oil from food waste with high energy density has potentiality of being a substitute for the fossil fuels (Chen et al., 2019).

Before using bio-oil as a drop-in fuel, upgrading is typically needed (Taghipour et al., 2019). The physical properties of bio-oil such as density, acidity, viscosity and chemical compositions are challenging problems in bio-oil applications including transportation fuels (Yang et al., 2015b). Moreover, the large amount of protein in biomass brings much N in the bio-oil, resulting in nitrogen oxide emissions during bio-oil combustion and deactivation in crude oil refineries (Du et al., 2012). There are many ways to improve the quality of bio-oil, such as catalytic cracking, separation, esterification, and hydrogenation (Ramirez et al., 2015). Solvent extraction needs several solvents to fractionate the oil product depending on the molecular characteristics of components (Ramirez et al., 2015), which makes the upgrading processes more complex. Distillation, another separation process, is not suitable for HTL bio-oil with irregular density (Taghipour et al., 2019). Hydrogenation can improve the heating value of bio-oil but make the viscosity unstable (Jena and Das2011; Taghipour et al., 2019). Disadvantages of catalytic cracking are low yields and easy coking for the upgrading of bio-oil (Srinivas et al., 2000). All the methods mentioned above require a deep-processing with more input of energy, materials and facilities. An upgrading method by the application of additives during the HTL process of bio-oil can improve the quantity of bio-oil simply and facilitate subsequent processing. Some research has been done about the production and upgrading of bio-oil via HTL of KW and other biomass waste. For the HTL of blackcurrant pomace, bio-oil yield was increased by recycling the process water – the bio-oil yield increased from 26 percentage weight (wt%) to 31 wt% and the energy recovery increased from 48% to 57% (Deniel et al., 2016b). A positive result of a decrease in the oxygen/carbon (O/C) ratio with fewer reductions in the hydrogen/carbon (H/C) ratio was achieved by using phosphoric acid and sodium hydroxide (NaOH) in the study of HTL of faeces and KW (Posmanik et al., 2018). The enzymatic pre-treatment of KW contributed the organic compounds analysed by gas chromatography (GC) in the bio-oil, reflecting an improvement in oil quality (Kaushik et al., 2014). The addition of a strong base in the hydrothermal conversion process of beech wood slightly increased the oil yield but at the same time improved the viscosity of the oil, which was not sufficient (Haarlemmer et al., 2016). Biomass and agriculture products are promising assets from an economy perspective. Agriculture companies in the Czech Republic were studied by Kohonen networks and show very favourable values—optimal assets level (Stehel et al., 2019). The profit or loss for ordinary activities is the main value generator and deserves much attention for economic analysis and the products of coke and bio-oil are very advantageous (Machová et al., 2018).

Previous studies have shown that KW has the potential to produce bio-oil from hydrothermal processes (Chen et al., 2019; Kaushik et al., 2014). Water-soluble additives have a positive effect on the HTL of biomass (Haarlemmer et al., 2016; Posmanik et al., 2018). However, the influence of different key reaction parameters (temperature and reaction time) on the quality of hydrothermal oil from KW has not been studied in detail. In addition, the study on the KW-based bio-oil upgrading by water-soluble additives is relatively lacking. This research studied the effects of temperature and reaction time on the quality of hydrothermal oil of KW, and gave the optimized conditions from the perspective of bio-oil quality. The effects of different water-soluble additives (hydrogen chloride (HCl), NaOH and iron(III) (Fe^{3+})) on the HTL bio-oil were compared in terms of yield, element distribution, molecular properties and viscosity. There is still no industry HTL application of KW. This research provided the optimistic HTL treatment parameters and analysed the component of bio-oil, which is good for its further application. A simple method to upgrade bio-oil was studied which can promote the bio-oil economic value.

Materials and methods

Materials

The KW was collected in the Zhejiang University canteen, located in Hangzhou, PRC. We collected the waste from the canteen waste can twice a day, continuously for 5 days in autumn. As shown in Online Supplementary Figure S1, after removing impurities such as large bones, plastics, metals, and wood, the dried solid KW was ground by a 4.5 kg rotary blade crusher and again placed in a 105°C for 24 hours in an oven. Then it was stored in a

Table 1. Analysis of characteristics of dry basis kitchen waste particles.

Elemental analysis/percentage weight (wt%)					
Carbon (C)	Hydrogen (H)	Oxygen	Sulphur	Nitrogen	H/C ratio
55.55	7.42	28.80	0.59	2.81	1.603
Proximate analysis/wt%				Higher heating value/MJ/kg	
Ash	Volatiles	Fixed C			
4.83	80.95	14.22		18.96	
Typical component ratio of dry basis/wt%					
Carbohydrate	Protein	Lipid			
48.02	18.76	28.39			

4°C refrigerator for further use. The characteristics of the KW particles after dried treatment are shown in Table 1.

Hydrothermal treatment and calculation methods

The HTL processes of KW were performed using a 500 mL Hastelloy C276 autoclave purchased from Parr Instruments with a heating rate of 15°C min^{-1}, as shown in Online Supplementary Figure S2(A). 30 g KW and 240 mL deionized water was loaded for all the tests. The reaction temperature range was from 260°C to 360°C with an interval of 20°C, and the residence time was 0 minutes, 20 minutes, and 40 minutes. Since the heating rate of the reactor is 15°C min^{-1}, it takes about 15 minutes to 25 minutes to rise the temperature from room temperature to the conversion temperature. Therefore, the residence time was set to 0 minutes to study the effect of the heating process on the hydrothermal reaction.

The experiments of upgrading with additives were performed at 5 mL 316 titanium alloy stainless steel reactors with a heating rate of 40°C min^{-1} by a GC oven, as shown in Online Supplementary Figure S2(B). The reaction temperature was set to 320°C and the residence time was 20 minutes. Ratios of alkaline, acidic and iron (Fe)-containing additives to KW (mol/kg) were 5, 2.5, and 1.25, and tests were noted as AL5, AL2.5, AL1.25, AC5, AC2.5, AC1.25, IC5, IC2.5, and IC1.25, respectively. With the ratio of Fe-containing additives to KW 2.5, IAC0.5, IAC1 and IAC2, these were the tests in which ratios of Fe^{3+}(mol)/H^{+}(mol) were 0.5, 1, and 2, respectively.

Dichloromethane (CH_2Cl_2) was added according to the ratio of 1/30 g/ml of KW and CH_2Cl_2 for extraction. Coke was filtered and washed by CH_2Cl_2. After the separation of oil and water, the bio-oil phase was dissolved in CH_2Cl_2, and the bio-oil phase and the coke phase were placed in a 45°C oven to remove the solvent to obtain bio-oil and coke products.

The product yield of the oil and coke phase were calculated according to Equations (1) and (2). Due to the presence of the additive, there are certain hetero atoms in the oil and coke phase which affect the true yields. Therefore, the yields after the ash removal was calculated in order to reflect the true yield results:

$$\textit{oil phase product yield without ash} = \frac{mass_{oil} \times 1 - mass_{ash}}{mass_{feedstock}} \times 100\% \quad (1)$$

$$\textit{coke phase product yield without ash} = \frac{mass_{coke} \times 1 - mass_{ash}}{mass_{feedstock}} \times 100\% \quad (2)$$

The calculation for oil phase and coke phase element recovery was performed using Equation (3):

$$\text{X recovery}(\%) = \frac{\text{percentage of X in phase} \times \text{phase weight}}{\text{percentage of X in feedstock} \times \text{feedstock weight}} \times 100\% \quad (3)$$

Characterization of HTL production

Elemental analyses (C, H, N, O, and Sulphur (S)) were characterized by a Thermo NA 2100 elemental analyser where the O element content was calculated by the difference method.

First, the digestion process was carried out – 5 mL of hydrogen peroxide and nitric acid mixed solution (1:1, mL: mL) was added to 80 mg of oil product, mixed well, put in water bath and warmed up to 90°C for 2 hours. After digestion, the solution was subjected to inductively coupled plasma mass spectrometry analysis in a Thermo Scientific XII analyser to analyse the metal element content of the bio-oil phase.

Boiling points of bio-oil components were analysed by a thermogravimetric analyser (TGA/SDTA851, Swartzer Land). Before the experiment, high-purity N was used first as a carrier gas to fully purge, weigh 6 mg of the sample in an electronic balance scale in a 0.1 mL alumina crucible, and then under a high-purity N atmosphere the increase in the temperature was from 30°C to 800°C at a constant heating rate of 10°C•min^{-1}. The experimental atmosphere was high-purity N (99.9999%) and the protective atmosphere N flow rate was 20 mL/min.

Calorific value measurement was carried out in a fuel characteristic analysis system 5E-IRSII (Kaiyuan Instrument Co., Ltd., PRC) following the Chinese National standards GBT 384-1981 and GBT213-2008.

The stress/strain experiments and rheological properties of the bio-oil phase product were analysed using a parallel plate rotational rheometer (ARES-G2, TA Instruments) with a diameter of 20 mm. The viscosity was measured at 60°C and a shear rate of 60 rad•s^{-1} was recorded. These tests followed the Chinese National standard GB/T 265-1988.

Table 2. Element analysis, calorific value of bio-oil and production yields.

Reaction parameter	Element analysis (%)					Higher heating value (MJ•kg^{-1})	Energy recovery rate (%)	Bio-oil yield (%)	Coke yield (%)
	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen				
Effect of reaction temperature (residence time was 20 minutes)									
260°C	68.61	9.49	2.56	0.26	19.08	33.20	65.32	37.3	24.8
280°C	68.84	10.03	2.35	0.26	18.52	36.82	87.58	45.1	11.5
300°C	70.18	9.38	2.34	0.44	17.66	37.23	84.82	43.1	11.2
320°C	71.67	9.00	2.42	0.26	16.65	37.75	85.81	43.2	10.6
340°C	72.27	9.16	2.59	0.24	15.74	37.70	90.06	45.3	9.8
360°C	71.58	8.95	2.56	0.27	16.64	38.09	89.60	44.7	8.7
Effect of residence time (temperature at 320°C)									
0 minutes	73.01	8.86	2.69	0.23	15.21	37.34	84.68	42.7	10.8
20 minutes	71.67	9.00	2.42	0.26	16.65	37.75	85.81	42.9	11.2
40 minutes	71.58	9.09	2.35	0.26	16.72	37.91	87.18%	43.2	10.1
60 minutes	72.24	9.42	2.54	0.27	15.53	38.02	86.04%	42.0	11.3

Statistical analysis

The product yields and element data measured from HTL of KW were submitted to analysis of variance. The Tukey test with a significance level of 5% was applied to deal with the notable abnormal situations and the comparison of the effectiveness of upgrading. The software used was MATLAB 2019b.

Results and discussion

Product analysis of HTL bio-oil via KW

The yields of coke and bio-oil are listed in Table 2. At the lowest conversion temperature of 260°C, the bio-oil yield is as low as 37.3%. The coke yield is 24.8%, which is the highest. At 280°C, the product oil yield increased to 45.1% while the coke yield suddenly reduced to 11.5%. At temperatures ranging from 280°C to 360°C, the oil yield fluctuated slightly from 43.1% to 45.3% and the coke yield decreased from 11.5% to 8.7%. The bio-oil yield change is owing to the incomplete hydrolysis of KW organic matter under low temperature, which affects the synthesis of bio-oil products (Malins, 2017). As the temperature rises, carbonization degree and various degradation reactions can be enhanced leading to the low coke yield (Reza et al., 2014). As for the residence time, it had a relatively small effect on the yields.

With the rise of temperature, the content of C and H in the bio-oil from HTL increased significantly while the content of S and O decreased. As the temperature increases, O is removed by decarboxylation during HTL and there is more C and H content in bio-oil (Zheng et al., 2015). However, the content of N did not change too much. The N in bio-oil mainly is the polycyclic nitrogenous compounds that come from the Maillard reaction between amino acids, and reducing sugars from the hydrolysis of proteins and carbohydrates in KW (Toor et al., 2011; Yang et al., 2015a).

The molecular properties of bio-oil refer to the boiling point (bp) classification of petroleum products by Speight: light naphtha (bp$<$149°C), medium naphtha (bp from 149°C to 232°C), gas oil (bp from 232°C to 343°C), light vacuum gas oil (bp from 343°C to 371°C), heavy vacuum gas oil (bp from 371°C to 566°C), and residuum (bp $>$ 566°C) (Speight, 2015). This bp classification method was also widely used in the analysis of other HTL oils (Déniel et al., 2016a; Ramos-Tercero et al., 2015; Zhu et al., 2015). The analysis results are shown in Online Supplementary Figures S3 and S4. The bio-oil at temperature of 260°C with far fewer light components and more heavy components is quite different from that of other bio-oils. The gas oil component has the highest content and together with light naphtha and medium naphtha, they are the main light component in the bio-oil accounting for about 60% to 70%. At 320°C, the light oil content is the highest. The content of the gas oil component is as high as 53.54%. The content of residuum is 12.39% which is the lowest. This result can be explained by excessive temperature causing the further hydrolysis of some small molecules to gas (Yang et al., 2015a). For the residence time, there is not a notable effect compared with temperature, which is consistent with previous HTL research results (Kim and Um, 2020).

A one-way correlation with the temperature between bio-oil viscosity and aqueous phase pH is illustrated in Online Supplementary Figure S5. As the temperature increased from 260°C to 360°C, the viscosity of the product oil decreased from 1.52 Pa•s to 0.71 Pa•s, and the pH of the aqueous phase increased from 4.48 to 7.75. Furthermore, as temperature increased, organic acids were consumed and pH increased. When the temperature reached 360°C, ammonia from the break-up of the amino-group made the pH higher than 7 (Yang and Yang, 2019). The high temperature hydrothermal condition can make the macromolecular organic matter in the raw material hydrolyse more thoroughly so that the light component in the bio-oil accounts for a higher proportion and the heavy component content decreases. Viscosity is the macroscopic physical property of the whole product oil, which is affected by many factors such as composition ratio, component bonding characteristics, component rheological properties, composition uniformity, internal friction strength, etc., and is macroscopically reflected as fluid viscosity. The viscosity of

the product oil decreased with the increase of temperature. The decrease of the heavy component content is one of the influencing factors.

The key parameters of hydrothermal reaction are reaction temperature and residence time. Too low reaction temperature will lead to insufficient hydrolysis of organic matter in raw materials resulting in lower oil yield, lower content of light components and higher viscosity (Malins, 2017). Excessive temperature can not only cause the light component content to drop slightly and the pressure to increase sharply but also result in a serious test of the safety and economy. The effect of residence time on the reaction is relatively small. Too short residence time may result in insufficient reaction between hydrolysis and condensation resulting in a decrease in oil quality. Excessive residence time increases the time and economic costs of hydrothermal reactions. Therefore, combined with the test results and comprehensive consideration of oil phase yield and quality, the safety and economy of the reaction process, the recommended optimal conditions for the HTL bio-oil production via the KW in this study are temperature 300–320°C, residence time 20–40 minutes, and reaction pressure 8–11 MPa.

Yield, element distribution and molecular analysis of upgrading

There is significant distinction in the effects of different additives on the yields. As shown in Online Supplementary Table S2, the increase of coke yield and decrease of bio-oil yield caused by alkaline additive indicates that alkaline additive can obviously promote the transfer of the bio-oil phase product to the coke phase. It is notable that the ash contents of coke are far higher than NA. During the HTL process, alkaline additive can influence hydrolysis, defragmentation, and other depolymerization reactions, forming different organic and inorganic salts in the coke phase, which reduce the bio-oil yield and increase the coke yield (Kim and Um, 2020; Malin, 2017).

Acidic additives have a certain effect on the improvement of both bio-oil and coke yield. The bio-oil and coke yields of AC5 are, respectively, 52.4% and 12.7%, which are 4.8% and 2.9% higher compared to the NA. As the proportion of acid additives decreased, the bio-oil yield decreased and the coke yield increased. The H^+ in acidic additives can promote the hydrolysis of materials in the initial stage of the hydrothermal reaction and increases the concentration of intermediate reaction monomers. Moreover, it can promote subsequent condensation and aromatization of pyrroles, esters and ketones so that the HTL process tends to produce more oil and coke phase product (Ross et al., 2010).

A significant effect on the improvement of bio-oil and coke yields emerges with Fe-containing additives. The oil phase and coke phase yields of IC5 are, respectively, 61.7% and 41.8%, rising to 14.1% and 32.0% higher than the NA. This may be due to the Fe element in the bio-oil and the coke phases. In order to investigate the effect of Fe on the yield of hydrothermal products, the elemental composition and ash content in the oil phase were analysed. Furthermore, the product yields after removing ash were calculated in order to give a more intuitive expression to the effect of additives.

Online Supplementary Table S1 shows the elemental composition and ash content of the products. It can be seen that the ash content in the non-additive oil phase is extremely low, while the high proportion additives, AL5, AC5, and IC5, can significantly increase the ash content as high as 3.27%, 4.88%, and 11.11%, respectively. The Fe-containing additive has the greatest influence on the ash content of the bio-oil. The oil phase yields of AL1.25, AC1.25 and and IC1.25 are, respectively, 42.0%, 45.7%, and 48.5%, close to oil phase yield NA. It can be visually seen from the Online Supplementary Table S2 that the alkaline additive can reduce the oil phase yield and increase the coke yield. The acidic additive has an effect on the improvement of both bio-oil and coke yields. The higher the ratio of acid additives is, the higher the oil phase yield and the lower the coke yield are. The fact that Fe-containing additives have a significant effect on the improvement of oil phase yield and coke yield is confirmed. As for the N content, the acidic additive can reduce it from 2.1(NA) to 0.5% (AC5), which is far more functional than the other two kinds of additives.

The recovery of Fe, carbon (C) and N in the HTL product are presented in Online Supplementary Figures S6 to S8. The recovery of Fe in the aqueous phase product ranges from 0.7% to 4.1%. The water-soluble Fe^{3+} ions are converted into water-insoluble substances and transferred to the oil and coke phase after HTL process. The C recovery rate of the bio-oil with alkaline additive is only between 33.4% and 53.9% which is much lower than that of NA oil phase due to the low bio-oil yields. Although the Fe-containing additive can improve the bio-oil yield, the C content is not high, resulting in the decrease of C recovery rates. Among all cases, only the acid additives tests (AC5 and AC2.5) have higher bio-oil C recovery rate than the non-additive bio-oil. Under acidic conditions, glucose is more likely converted to 5-hydroxymethyl-furfural (HMF) than short-chain carboxylic acids (Yin and Tan, 2012). As an important reactant for the production of dimethyl-furan as well as other biofuel precursors (Rosatella et al., 2011), more HMF can positively affect the HTL process and improve the bio-oil yield and C recovery rate (Posmanik et al., 2018).

All the three kinds of additives, alkaline, acidic and Fe-containing, can reduce the recovery of N of HTL bio-oil. The N contents in the oil phase were reduced to as low as 0.5%. The denitrification effect varies depending on the type and concentration of the additive. The sum of the recovery of N in the oil phase with alkaline additive in three phases is about 70–80%, lowest among the recovery rates of N in all elements. The ammonia gas from decarboxylation and deamination is a product during the HTL process of protein (Yang and Yang, 2019). Under alkaline hydrothermal environment, the amino group easily escapes in the form of a gas resulting in the low total recovery of N. Acidic additives can reduce the recovery of N more

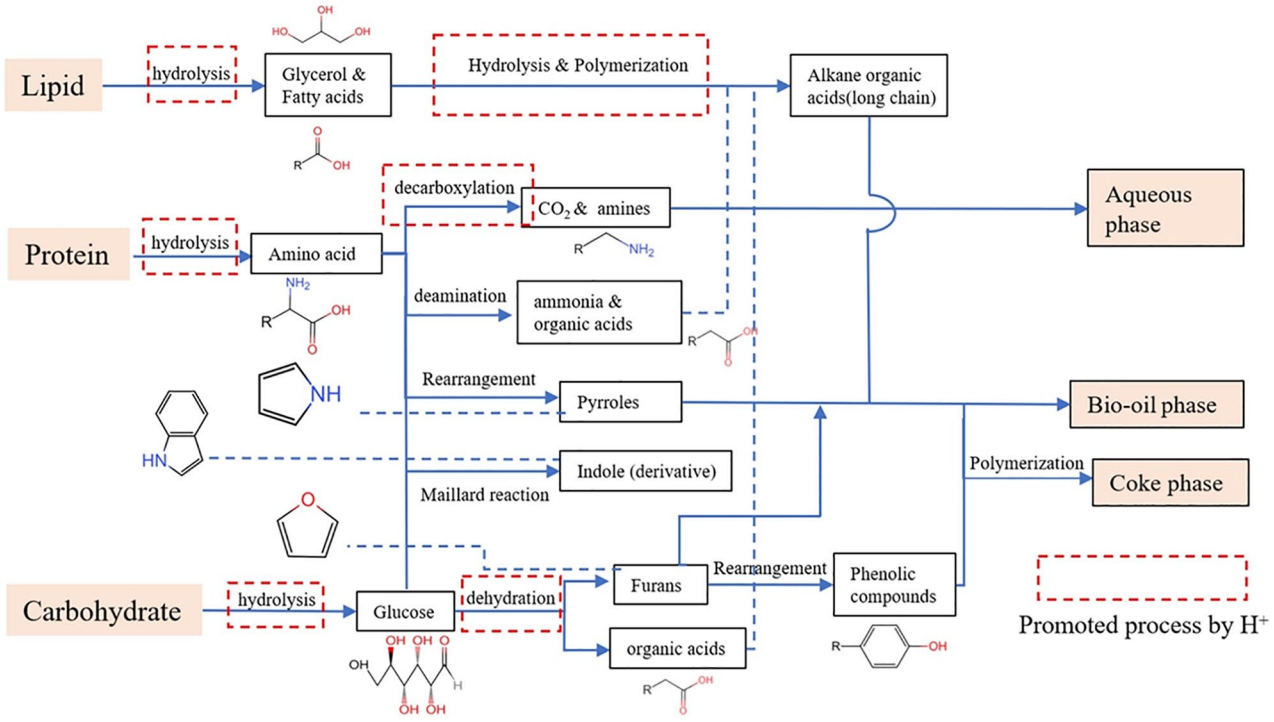


Figure 1. Schematic paths of the KW hydrothermal liquefaction process.

obviously. In tests AC5, AC2.5, and AC1.25, the content of N in the oil phase is 0.5%, 0.9%, and 1.5%, respectively. The recovery of N in the oil phase is 11.0%, 16.8%, and 26.1%. Both of these two indicators are lower than those of NA. The N recovery rate of the aqueous phase with the acidic additive is relatively high, up to 56.9%, which indicates that the N element is mainly transferred to the aqueous phase. N mainly existed in amino acids produced by proteolysis of proteins. There are two main paths for the reaction of amino acid: (a) deamination to produce ammonia and organic acids: and (b) decarboxylation to produce carbonic acid and amines (Toor et al., 2011). Under acidic conditions, amino acids are more likely to undergo decarboxylation reactions and N-containing organic compounds such as amines are dissolved in the aqueous phase (Ross et al., 2010). The effect of Fe-containing additive on the distribution of N is relatively weak. The N content and N recovery rate is higher than the tests with acid additive.

Schematic paths are shown in Figure 1. Lipid is mainly composed of triglycerides, which is hydrolysed to fatty acids and glycerol when the hydrothermal temperature is higher than 280°C. Organic acids and glycerol are further hydrolysed and polymerized to produce long chain organic acids of alkanes (Bühler et al., 2002). During the HTL process, proteins are hydrolysed to amino acids. Amino acids produce mainly amines and carbon dioxide through decarboxylation and fewer organic acids and ammonia through deamination (Yang and Yang, 2019). The type of HTL product of protein is related to the type of amino acid in protein. Various types of amino acids react to form pyrrole and indole substances. The HTL product of protein contains a large amount of N–O heterocyclic substances. Carbohydrates such as starch and cellulose are rapidly hydrolysed to produce oligosaccharides and glucose, which can further produce furan compounds through acid-catalysed dehydration under acidic conditions (Ross et al., 2010). Phenolic aromatic hydrocarbons generated by the secondary reaction of glucose can be polymerized to produce macromolecular oil products. When the aromatics in the solution reach the saturation critical value, crystal nuclei can be generated and grow to coke particles through diffusion and adsorption (Reza et al., 2014).

The molecular properties of different bp components of the oil phase product are presented in Online Supplementary Figure S9. Taking NA as reference, the content of light naphtha of the bio-oil with alkaline additive increased while the content of light vacuum gas oil component decreased. With regard to bio-oil with acid additive, the content of light naphtha and medium naphtha goes up. The content of residuum of the bio-oil with Fe-containing additive is significantly increased. The bio-oil residuum component is mainly composed of macromolecular colloid and asphaltene, while the Fe-containing compound is also mixed in the residuum. Therefore, the excessive content of residuum in the oil phase containing Fe additive may affect the evaluation of other components in the oil phase product. The ratio of light component to heavy component (excluding residuum) can be used to compare the quality of the oil with different additives. A ratio of light component to heavy component, ratio B, has been established as follows:

$$ratio\ B = \frac{fraction\ of\ (\text{light naphtha, medium naphtha, and gas oil})}{fraction\ of\left(\begin{array}{c}light\ vacuum\ gas\ oil\ and\\ heavy\ vaccum\ gas\ oil\end{array}\right)}$$

It can be seen from Online Supplementary Table S2 that the ratio with Fe-containing additive was improved compared with the non-additive oil phase, and the ratio can be up to 3.7. Acidic additives have the most significant increase in the ratio. The ratio B of the tests AC5 and AC2.5, and AC1.25 are as high as 9.4, 8.2 and 5.4, respectively.

Fluidity analysis of bio-oil

Online Supplementary Figure S10 shows the strain change over time with the same shear stress (stress = 10 Pa). Under the same shear stress condition, the slope of the strain represents the viscous strength of the bio-oil product and the higher the strain is, the closer the oil property is to the ideal liquid and the better the fluidity is (Girimath and Singh, 2019). The strains of the bio-oil with alkaline additive and acidic additive oil phase are higher than that of NA oil phase, which indicated that both the alkaline and acidic additive can improve the fluidity of the oil phase product. Conversely, the Fe-containing additive has a negative influence on the oil phase fluidity resulting in a lower curve of strain. The strain of the oil phase with acidic additive and the non-additive oil phase increased linearly with time expressing that the structure of the oil phase product is more uniform. It is interesting that the linear relationship with time of the strain of the bio-oil with alkaline additive is poor, which may be caused by the fine particles from reaction between the oil phase and the O in the air.

The oil product of HTL has a certain elasticity at normal temperature and is a typical viscoelastic fluid. The creep properties of the HTL bio-oil are displayed in Online Supplementary Figure S11. The shear strength of the different oil phase products was set to zero when the strain was 20%. The faster the recovery rate is, the higher the modulus of elasticity in the fluid is and the closer the fluid properties to the ideal solid properties are. The test results show that the recovery rate of bio-oil with acidic additive is the only one where the curve is lower than that of the NA bio-oil and is much smaller than that of bio-oil with Fe-containing additive and alkaline additive, which indicates that the oil phase still has a flow closer to the ideal liquid under creep conditions.

The effect of additives on the viscosity of bio-oil products can be observed from Online Supplementary Figures S12 to S15. The high proportion of alkaline additives (AL5 and AL2.5) made the static viscosity of oil phase go up to 87.6 Pa•s, a value close to asphalt. As discussed about Ratio B, lack of light component in bio-oil is the main reason causing the high viscosity. Although the low proportion of alkaline additive (AL1.25) reduces the dynamic viscosity effectively, it also has a poor phase uniformity problem. The low concentration of acid additive (AC1.25) has little effect on the viscosity. When the concentration of acid additive is up to 2.5 mol•kg^{-1} (AC2.5), the oil phase viscosity is significantly reduced with a viscosity similar to that of commercially available heavy diesel (Wang et al., 2020). Besides the reason that acidic additive can improve the content of light component in bio-oil, another explanation is that the acid can cause a decrease in electrostatic repulsion of fluid leading to lower viscosity (Li et al., 2019). However, the viscosity of AC5 is higher than that of NA. This may be explained by too much acid enlarging the deviation from the isoelectric point where the viscosity is the lowest (Franco et al., 2000). As for IC2.5 and IC1.25, its static viscosity is higher than that of NA. While the shear rate is higher than 100 s^{-1}, the oil phase viscosity is lower than that of NA. Fe-containing particles existing in bio-oil diminished with increasing shear rate and the particles move relatively to each other to orientate themselves in the direction of flow (Hiltunen et al., 2018). The effect of different acidity on the viscosity of the Fe-containing additive oil phase is not positively correlated and there is no obvious upgrading effect.

To summarize, with the concentration of acid additive to KW in the moderate range (2.5 mol•kg^{-1}), the oil phase viscosity can be lowered and the fluidity can be improved.

The fundamental reason for bio-oil property (for example, the viscosity) variation depends on the composition variation, and heavy components can negatively affect the viscosity (Kanaveli et al., 2017). The test with acidic additive, the best performed in this study, has a relatively consistent performance between the components and viscosity.

Conclusions

The HTL results of KW: the temperature had a greater effect on the yields and composition of the bio-oil than the reaction time. According to the oil quality and yield, the optimized working conditions for the HTL of KW are conversion temperature 320°C, and residence time 20 minutes, where the content of light component is highest.

Upgrading effect: appropriate proportion of acidic additive can effectively reduce the N content from 2.1% to 0.5% and improve the bio-oil yield. Alkaline additive has a negative effect on the bio-oil yield. Although the Fe-containing additive can increase the bio-oil yield, it increases the ash content.

The ratio of light component to heavy component can increase by up to 9.4 with high concentration of hydrogen chloride (HCl). Nevertheless, it can increase the oil viscosity. Among HCl, NaOH, and Fe^{3+} additives, only a ratio of 2.5 mol•kg^{-1} of HCl could reduce the bio-oil viscosity, which is close to commercially available diesel.

In conclusion, compared to alkaline additive and Fe-containing additive, a proper acidic HTL conversion condition can positively affect the HTL process of KW and upgrade the bio-oil in the aspects of yield, C recovery, N content, and fluidity.

Prospect: the synergies of protein, carbohydrate, and lipid during HTL have not been clarified. More kinds of additives/catalyst, such as precious metal additives and heterogeneous solid additives, can be analysed in the future. Also, more financial analysis should be carried out.

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