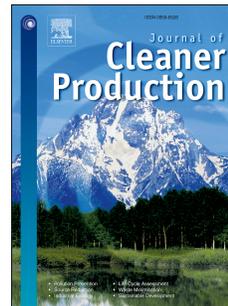


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Intermediate pyrolysis of organic fraction of municipal solid waste and rheological study of the pyrolysis oil for potential use as bio-bitumen

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Abstract

This work presents a study on intermediate pyrolysis of the organic fraction of municipal solid waste (OFMSW) and characterisation of organic liquid product (pyrolysis oils) with particular focus on aging and rheological characteristics. The feedstock was a real municipal waste sample received from a local waste treatment plant. Shredded into small particles, it contained a high amount of moisture (51.2%) and ash (17.4%). A pilot-scale intermediate pyrolysis system was used to process the material. The process mass balance showed that the yield pyrolysis oil was 10.6%. GC-MS and FTIR experiments showed that the accelerated aging (80°C for 24h) did not cause an obvious change in the liquid chemical composition, but led to a significant reduction in the solids and moisture contents. The dynamic viscosity tests demonstrated that the intermediate pyrolysis oil derived from OFMSW is a non-Newtonian fluid. The dynamic viscosity of the pyrolysis oil reduced with the increase of temperature or shear rate, which can be modelled by WLF function and the Carreau model, respectively. A shear rate-temperature superposition method was proposed to construct the viscosity master curve at a wide range of shear rate, where WLF function was employed to model the shear rate-temperature shift factor. The accelerated aging caused an obvious reduction in dynamic viscosity, resulting from the decomposition of the semisolid organic agglomerates in the solids content during the aging of the OFMSW intermediate pyrolysis oil. The relatively high viscosity and reduced viscosity after aging of the OFMSW pyrolysis oil has indicated its potential for application as a substitute of the light fraction in the bitumen for road construction.

Keywords: organic fraction of municipal solid waste; intermediate pyrolysis; pyrolysis oil; aging; dynamic viscosity; viscosity master curve

Abbreviations

ASTM	American Society for Testing and Materials
FID	Flame Ionization Detector
FTIR	Fourier-Transform Infrared Spectroscopy
GC-MS	Gas Chromatography–Mass Spectrometry
HHV	Higher Heating Value
OFMSW	Organic Fraction of Municipal Solid Waste
WLF	Williams–Landel–Ferry

1. Introduction

Pyrolysis is a thermochemical decomposition of organic material that occurs at moderate temperatures of 300-500°C in the absence of oxygen. Typically, there are three final product phases, namely pyrolysis liquid (consisting of an organic fraction and an aqueous fraction), permanent gases and char. Pyrolysis process has been applied for centuries in charcoal production, but only in the last 40 years has pyrolysis of biomass become of great interest; the biomass-derived liquid pyrolysis oil has strong potential in direct fuel application or as a source of high-value chemicals [1,2]. In waste

processing and management, pyrolysis was initially adapted to reduce the volume of solid waste and render its inert material. More recently, pyrolysis has been employed as a method for waste disposal and energy recovery [3]. There have been increasing research activities and industrial developments of pyrolysis of municipal solid waste (MSW) or refuse-derived fuel (RDF) by using a different type of reactors to produce pyrolysis oils [4,5].

The physical and chemical properties of pyrolysis oils determine their applications. Czernik and Bridgwater provided a comprehensive review relating pyrolysis oils' characteristics and application pathways [6]. The viscosity of a fluid is a measure of the resistance (originated from the internal structure and molecular interactions of a fluid) to gradual deformation by shear stress or tensile stress. It is a significant physical property, as it essentially determines the flow characteristics of a fluid in a certain temperature and therefore affects the handling methods applied for storage and transportation etc. [7] The viscosity is also of great interest when the pyrolysis liquid is used as a component or an alternative to the binder in construction material, such as bio-bitumen, as it will affect the blending temperature of the mixtures. The viscosity of pyrolysis oils as produced can vary significantly; it is largely dependent on the type of feedstock and processing technology that results in the content of water and light fraction in the liquid [1].

Rheology applies to a fluid that has a complex structure and its flow behaviour cannot be characterised by a single value of viscosity, since the viscosity changes with temperatures and shear rates. There has been some research to address the viscosity or rheological study of different pyrolysis oils. For example, Nolte and Liberatore [8] analysed the rheological property of a set of pyrolysis oil samples derived from woody and grass biomass feedstocks by the fluidised bed, vacuum and vortex pyrolysis reactors. It was found that most of the pyrolysis oil samples were Newtonian under most testing conditions, but some hardwood pyrolysis oils sheared thin at low temperature (-5°C) and high shear rate ($>100\text{ s}^{-1}$). It is also concluded that the two major factors that affected the pyrolysis oil viscosity were the temperature and the liquid moisture content. Jampolski [9] studied the viscosity of aged pyrolysis oils produced in a screw reactor from various feedstocks including beech wood, wheat straw, chicken manure, and sewage sludge. The viscosity measurement was taken between 20 and 80°C . Three of the pyrolysis oil samples presented Newtonian flow behaviour in the measured temperature range, but wheat straw pyrolysis oils were non-Newtonian at temperatures below 50°C . Zhang et al [10] studied the dynamic viscosity of fast pyrolysis oil and bio-slurry (a blend of pyrolysis oil and bio-char). The results showed that the addition of bio-char (up to 20%) in pyrolysis oils could decrease the dynamic viscosity of the liquid in 40°C , but the liquid remained as a Newtonian fluid. Cai et al [7] studied the rheology of four aged bio-oil samples from fast pyrolysis of miscanthus and beech wood at various shear rates and temperatures by using a rotational viscometer. All the pyrolysis oil samples maintained constant viscosity at various shear rates at the same temperature, which indicated their Newtonian characters. The Williams-Landel-Ferry (WLF) model was used to model the viscosity-temperature relationship and the results showed a close fit between the modelling and experimental data.

This work presents the mass balance of pilot-scale intermediate pyrolysis of organic fraction of municipal solid waste (OFMSW) and the characterisation of pyrolysis oil with particular interests in its aging and rheology. Neither of these works has been reported in the literature. Particularly it was not found for the rheological modelling for the temperature- and shear rate-dependent viscosity of the pyrolysis oils from OFMSW. Thus the rheological characteristics of both fresh and aged pyrolysis oils were analysed and compared in this study. Gas chromatograph-mass spectrometer (GC-MS) and Fourier Transform-Infrared (FTIR) analyses and solids content measurement of the pyrolysis oils were compared before and after the accelerated aging of the pyrolysis oils, which were used to support the analysis of the rheological study. A master curve for the viscosity of the pyrolysis oils was constructed to characterise its temperature and shear rate dependence based on WLF function.

2. Material and Methods

2.1. Feedstock

The OFMSW feedstock used in this work was provided by a municipal waste treatment plant in Leicester, UK. It was originally collected from households and later processed at Material Recovery Facilities (MRF) for recovering recyclable materials. The remainder contains a small amount of organic fraction, such as decomposed food, papers, textiles, plastics, wood, and most of the inert

material in the MSW. This material was further shredded to reduce the particle size to less than 10 mm for use in the pyrolysis experiments.

The proximate and ultimate analyses of the feedstock are shown in Table 1 and the compositional analysis is shown in Table S1. The results show that feedstock, as received, has a very high moisture content (51.2%), which is likely resulted from the water produced during the food waste decomposition and water absorbed from the environment during the waste collection and storage. This result is consistent with the works reviewed by Chen et al [4,11]. The content of ash and inert material in the feedstock accounts for 17.4% on a wet basis.

Table 1. Proximate and ultimate analysis of OFMSW feedstock

	Measure	Value
Ultimate Analysis ¹⁾		
C	wt.%	62.0%
H	wt.%	8.4%
N	wt.%	2.9%
S	wt.%	0.8%
O ²⁾	wt.%	25.9%
Proximate Analysis ³⁾		
Moisture	wt.%	104.9%
Volatiles	wt.%	59.6%
Fixed Carbon	wt.%	4.7%
Ash Content	wt.%	35.7%
HHV	MJ kg ⁻¹	15.4

1) Ultimate analysis is presented on dry and ash free basis,

2) Oxygen content was calculated by difference

3) Proximate analysis is presented on dry basis

2.2. Intermediate Pyrolysis

The intermediate pyrolysis system was developed at Aston University in 2008 [12]. The reactor is a horizontal cylindrical reactor and uses screw conveyers to transport and circulate the feedstock inside the reactor. The pilot-scale reactor used in this work is heated externally by electrical heating units. It has a length of 180 cm and a diameter of 20 cm with a designed maximum feedstock of 20 kg h⁻¹. The unique feature of the reactor is that there are two co-axial screw conveyers located inside the reactor. During operation, the inner screw conveys a mixture of fresh feedstock and recycled char product forward through the reactor, and the outer screw returns a portion of the char product backwards to achieve internal char recycling. Hot char performs as an effective heat transfer medium as well as a catalyst for thermal cracking, in particular when the high-ash content feedstock is processed [12]. Due to the advantages of auger screw arrangement, this reactor can effectively process various type of biomass feedstocks, in particular difficult organic waste materials, such as MSW, sewage sludge, paper processing waste in the form of large particles and pellets [13,14].

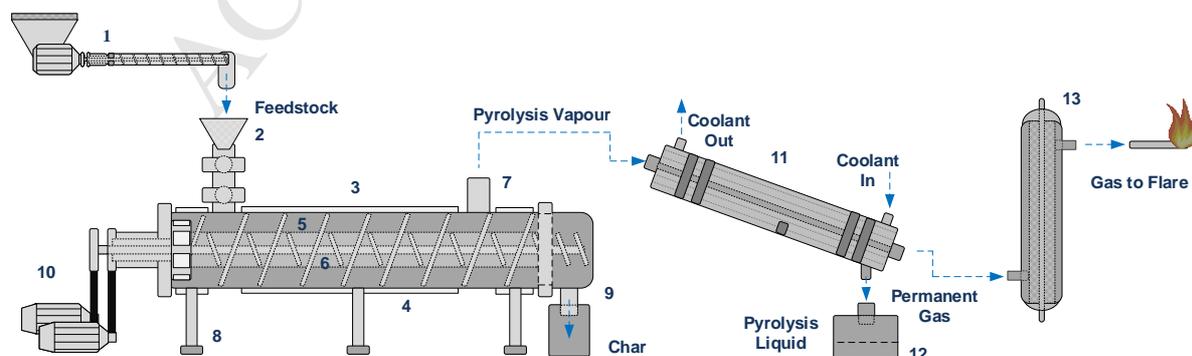


Figure 1. Schematic diagram of the intermediate pyrolysis system

(1) Feeder; (2) Feed Inlet; (3) The Pyrolysis Reactor; (4) Heating Jackets; (5) Outer Screw; (6) Inner Screw; (7) Vapour Outlet; (8) Stands; (9) Char Outlet And Char Pot; (10) Motor; (11) Shell and Tube Condenser; (12) Liquid Vessel; (13) Electrostatic Precipitator

The full illustration of the intermediate pyrolysis system is shown in Figure 1. The system comprises a screw feeder, a pyrolysis reactor, a shell and tube water-cooled condenser and an electrostatic precipitator (ESP). The screw feeder continuously feeds the material through an evacuation-valve-controlled feeding chute. The pyrolysis vapour leaves the reactor and passes through a shell and tube condenser, where the pyrolysis vapour is condensed in the heat exchanger to form pyrolysis liquid. The permanent gases pass through the ESP system for aerosol removal. After some additional fibre cartridge filtration, the final cleaned gas is sent to the flare system. Char from the pyrolyser is collected in a char pot. In the intermediate pyrolysis process, the liquid product is usually produced in a separated aqueous fraction and an organic fraction. This is owing to the screw configuration that allows prolonged solid residence time in the reactor and extended involvement of char in the pyrolysis process, which can lead to promoted secondary reactions. This results in lower molecular weight components in the organic fraction with considerably lower water content. The typical product yields of intermediate pyrolysis of biomass are approximately 50% liquid, 30% solid and 20% gases. It is worth noting that the product distribution is heavily depended on the feedstock characteristics and the processing conditions [12,13].

Before a run, the pyrolysis reactor was gradually heated to 500°C and held at that temperature for 30 minutes. The full heating process took approximately 2.5 hours. The rotating screws were also turned on during the heating phase and the speed of the inner screw and outer screw were set to 1 rpm and 6 rpm, respectively. This gave a solid residence time of approximately 1.5 minutes. A nitrogen purge was used to eliminate any presence of air inside the reactor. When the reactor was ready, the OFMSW feedstock was continuously fed into the reactor at a rate of 1.6 kg h⁻¹ by a screw feeder. The reactor was not able to achieve a full feeding load, as the bulk densities of the feedstock were relatively low and attempts to feed at a higher rate resulted in blockages in the feeding chute. As soon as the material was fed, smoke immediately appeared in the liquid collection bottle. The liquid product generally starts to appear after 10 minutes. Nitrogen purge will be terminated as soon as this happens. The process took one hour to reach steady state (constant temperature and char production rate), after which steady-state conditions were maintained for a minimum of one hour. Mass balance (weight percentage on a wet feed basis) was calculated based on the masses of feedstock processed and final products of pyrolysis liquid (oil and water fraction) and char. The yield of permanent gas was calculated based on the gas flow measurement and gas composition. In the present work, nine pyrolysis experiments were performed with a total of 49.21 kg consumed.

2.3. Pyrolysis Oil Characterisation

The elemental composition analysis was carried out using a Thermo Scientific FLASH 2000 elemental analyser. The contents of carbon, hydrogen, nitrogen and sulphur were analysed in triplicate and average results were taken. The content of oxygen was calculated by difference.

The chemical analysis of the liquid sample was carried out by using a Varian 450 gas chromatograph (GC) coupled to a Varian 220 mass spectrometer (MS) with a flame ionisation detector (FID) and an Agilent J&W VF-5ms column (L: 30 m, ID: 0.25 mm and DF 0.25 µm). Helium was used as the carrier gas and GC grade acetone was used as the dilution solvent. The GC injection port was maintained at 275°C and the oven was heated at 5°C min⁻¹ from 45°C to 280°C. The FID detector was held at 275°C. Proposed assignments of peaks from the analysis chromatograph were made based on mass spectra from the NIST 2011 MS library.

In order to qualitatively identify the vibrational bands in both fresh and aged pyrolysis oils, FTIR spectroscopy test was carried out by using a PerkinElmer spectrum 100 spectrometer. The device was set to scan in range of (4000-4500) cm⁻¹, with a scan number of 16 and 4 cm⁻¹ resolution. The samples were prepared by dissolving pyrolysis oil in equal amounts by weight of acetone in a closed container. A thin layer (< 0.2 mm) of the dissolved sample was placed on a sodium chloride plate and left until the solvent completely evaporated leaving only the pyrolysis oil, then the plates were scanned in the spectrometer. In order to ensure the accuracy of the results, the tests were performed in duplicates and the dichloromethane solvent was used instead of the acetone for further examination for any difference caused by the solvent.

The density of the pyrolysis oil was measured by using a Mettler Toledo 30PX densitometer. Samples are injected into a measuring cell and the device calculates the liquid density by measuring the light reflection from the liquid surface.

The water content of the pyrolysis oil was determined by using a Mettler Toledo V30 Compact Volumetric Karl Fischer (KF) titrator in accordance with ASTM E203. Due to high viscosity, the pyrolysis oil samples were diluted with acetone in approximately 1:4 mass ratio prior to analysis. The water content results were corrected to weight percent of the original oil sample.

The higher heating value (HHV) of the pyrolysis oil was determined by using a Parr 6100 calorimeter in accordance with ASTM D420. Weighted liquid samples are placed in a Parr 1108 combustion bomb and ignited by heating wires in an oxygen-enriched environment. The system automatically logs the temperature increase in the combustion bomb and calculates the gross heating value of the weighed sample.

Determination of solids content in the pyrolysis oil was carried out in accordance with ASTM D7579. A representative sample of pyrolysis liquid was dissolved in Methanol-dichloromethane solvent. The solution was filtrated through a 1 μ m pore size fibre filter. After filtration, the filter paper with the residue is air-dried for 30 minutes. The solids content is calculated by the weights of dry solids and the original pyrolysis liquid sample.

2.4. Accelerated Aging

To understand the change of composition and properties in pyrolysis oil over a storage period, the accelerated aging experiment was performed on the pyrolysis oil samples. There is no established standard method for pyrolysis oil aging, but Oasmaa et al [15] developed a general protocol for fast pyrolysis oil, which has been frequently applied in relevant research [16]. This method was adopted in the present work.

In order to ensure the tested pyrolysis oil is relatively homogeneous, 200 ml of oil sample was heated to 40°C and well mixed manually. The sample bottle was then left to stand for 2 hours. When all air bubbles disappeared, the liquid sample was poured into a 50ml steel vessel. The vessel was sealed and then placed in an oven for a heating at 80°C for 24 hours. For conventional biomass-derived fast pyrolysis oil (bio-oil), this selected accelerated aging condition is considered to be equivalent to a 6-month aging in ambient conditions [16].

2.5. Rheological Analysis

The rheology of the pyrolysis oil is characterised by its dynamic viscosity, which is measured by using a Brookfield rotational viscometer (model: DV-II+ Pro). A water-bath based temperature controller (model: Thermo Haake Phoenix) was employed to control the temperature of the pyrolysis oil sample. Brookfield Rheocalc software was used to control the test and record the data. The viscometer measures the torque required to maintain the rotation of a spindle in the fluid of interest at a specific rotational speed. The shear stress (Equation 1) is linearly proportional to the torque and inversely proportional to the spindle surface area. The shear (strain) rate (Equation 2) of the liquid sample is linearly related to the rotational speed and calculated as a function of the spindle radius, container radius and the rotational speed. Then the dynamic viscosity of the liquid is calculated as the ratio of the shear stress to the shear rate with a unit of Pa·s, shown in Equation 3.

$$\tau = \frac{T}{2\pi R_s^2 L} \quad (1)$$

$$\dot{\gamma} = \frac{2\omega R_c^2 R_s^2}{x^2(R_c^2 - R_s^2)} \quad (2)$$

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (3)$$

where η is dynamic viscosity (Pa·s); τ is share stress (N (cm²)⁻¹); $\dot{\gamma}$ is share rate (s⁻¹); T is torque (N·m); L is effective spindle length (m); R_s is spindle radius (m); R_c is container radius (m); ω is rotational speed (rps) and x is radial location where share rate is being calculated (m).

To evaluate the temperature dependence, the dynamic viscosity of the pyrolysis oil was measured at 40, 50, 60, 70 and 80°C, respectively. These temperatures were selected based on 1) the different temperatures needed to characterise the temperature susceptibility of the viscosity of the pyrolysis oil; 2) the selected temperatures that represent the high-temperature conditions for asphalt roads when using the pyrolysis oil as a bio-bitumen component in asphalt; and 3) a higher temperature (e.g., greater than 100°C) is not recommended for the pyrolysis oil due to concerns over the oil's thermal stability. The water bath was used to maintain the sample temperature with an accuracy of ± 0.1 °C.

At each testing temperature, the shear strain rates of 0.2, 0.5, 1, 2, 5, 10 and 20 (unit: s⁻¹) were respectively employed to evaluate the shear rate effect on the dynamic viscosity of the OFMSW pyrolysis liquid. The spindle rotational speed was adjusted to achieve the above shear rates. Spindles with different radii were used to ensure that the torque was maintained above 10% of the torque capacity of the viscometer. At each specific temperature and shear rate, the test was continued for 20 minutes or terminated until a stable viscosity was reached (i.e. no significant variation was found for the viscosity with testing time). Each viscosity measurement was performed in triplicate and average results were reported.

2.5.1 Temperature dependent viscosity models

To evaluate the temperature dependence of the dynamic viscosity of the OFMSW pyrolysis oil, two rheological models are used including Arrhenius model in Equation 4 [17] and the Williams-Landel-Ferry (WLF) model in Equation 5 [18].

$$\eta_T = \eta_0 e^{\frac{\Delta E}{RT}} \quad (4)$$

$$\eta_T = \eta_0 e^{-\frac{C_1(T-T_0)}{C_2+(T-T_0)}} \quad (5)$$

Where η_T is the dynamic viscosity at absolute temperature T (K); ΔE is an activation energy (J mol⁻¹); R is gas constant = 8.314 J mol⁻¹K⁻¹; C_1 and C_2 are the coefficients of the WLF model; T_0 is a reference temperature (Kelvin), which is treated as an adjustable parameter; η_0 is the viscosity at a specific temperature, e.g. the infinite temperature for Arrhenius model and the reference temperature for WLF model. Thus η_0 are different values for the Arrhenius and WLF models. It is noted that η_0 , T_0 , C_1 and C_2 in the WLF model are empirical parameters and only three of them are independent. The higher the C_2/C_1 value, the lower the dependence of viscosity with the temperature. The Arrhenius model has been used to characterise the temperature dependent viscosity of the various bio-oils from woods [19] and switchgrass [20]. It is not clear that which model (Arrhenius or WLF model) is applicable to model the temperature dependence of the viscosity for the OFMSW-derived pyrolysis oil, hence this is one of the objectives to be examined in this work.

2.5.2 Shear rate dependent viscosity model

To evaluate the strain rate effect on the viscosity, the pyrolysis liquid is hypothesized as a Carreau type fluid, which is a non-Newtonian fluid (proved to be true based on test results in the next section). The Carreau type fluid has a constitutive equation following a generalised form of Newtonian fluid that is $\tau = \eta(\dot{\gamma})\dot{\gamma}$ and the strain rate dependent viscosity is expressed by Carreau model as [21]:

$$\eta(\dot{\gamma}) = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{[1 + (\lambda\dot{\gamma})^2]^n} \quad (6)$$

where η is viscosity (Pa·s); η_{∞} is viscosity at infinite shear rate (Pa·s); η_0 is viscosity at zero shear rate (Pa·s); λ is relaxation time (s); $\dot{\gamma}$ is shear (strain) rate (s^{-1}) and n is a power index.

3. Results and Discussion

3.1 Mass Balance

Figure 2 shows the overall mass balance of the intermediate pyrolysis runs on dry feed basis. The yields of organic liquid (pyrolysis oil), aqueous liquid (reaction water), permanent gas and char are 10.6, 7.5, 23.2 and 51.7 wt.%, respectively. The mass balance closure is 93.0%, which is highly satisfactory for a pilot-scale experiment. It is worth noting that the aqueous product presented only accounts for the reaction water produced in the pyrolysis reaction. Moisture from feedstock is not counted as a product. The same applies to other intermediate pyrolysis tests [13,14]; there is a clear phase separation between the organic and aqueous products. A wax-like viscous organic fraction (pyrolysis oil - see Figure S2) floated on top of the aqueous fraction. Char is the highest yield product since it contains all the inert material and ash from the feedstock. The yield of organic pyrolysis oil was 10.6%. In addition to the relatively low yield, the high viscosity of the pyrolysis oil (will be discussed in Sections 3.3–3.5) also caused difficulty in collection. The loss shown in the mass balance is largely due to the loss of pyrolysis oil in the condenser inner wall and related pipework.

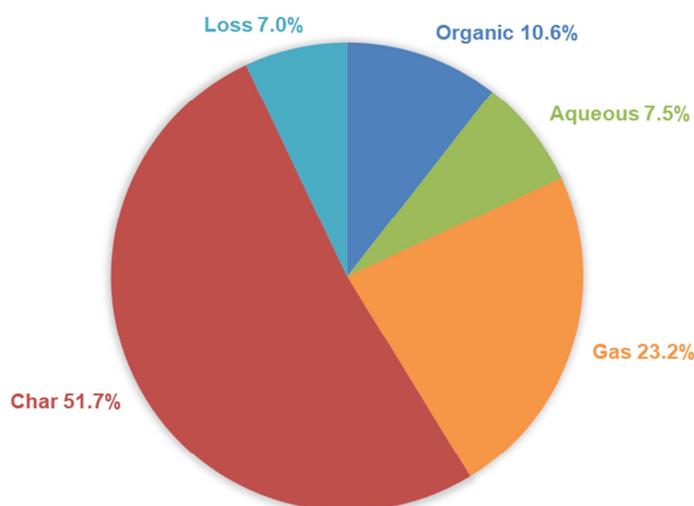


Figure 2 Mass balance of the pyrolysis process (dry basis)

3.2. Pyrolysis Liquid Characterisation

3.2.1. Compositional analysis

The gas chromatograms of the pyrolysis oil before and after the accelerated aging test are presented in Figure 3 and a list of identified chemical compounds are presented in Table S2. In comparison, there is no apparent difference between the two chromatograms in peak number, peak location and their abundance, which indicates that the chemical compositions of the pyrolysis oil remain the same before and after aging. This provides evidence that this accelerated aging condition did not cause any obvious changes to the intermediate pyrolysis oil in terms of chemical composition. In other words, this pyrolysis oil has a very stable composition. From Table S2, it can be concluded that the pyrolysis oil consists of mainly major chemical groups, namely heterocyclic, benzene (including phenolic) based and long-chain aliphatic compounds, which are derived from various parts of the feedstock,

including lignocellulosic biomass, plastics and animal fat. Conventionally, biomass-derived pyrolysis oil (particularly fast pyrolysis oil) is unstable, as it contains a high amount of reactive oxygenated compounds and low boiling organics from primary pyrolysis [19]. However, in intermediate pyrolysis, the reactor provides prolonged solid and vapour residence time, which ensures maximised secondary reactions (such as cracking and reforming) in pyrolysis and forms more stable chemicals.

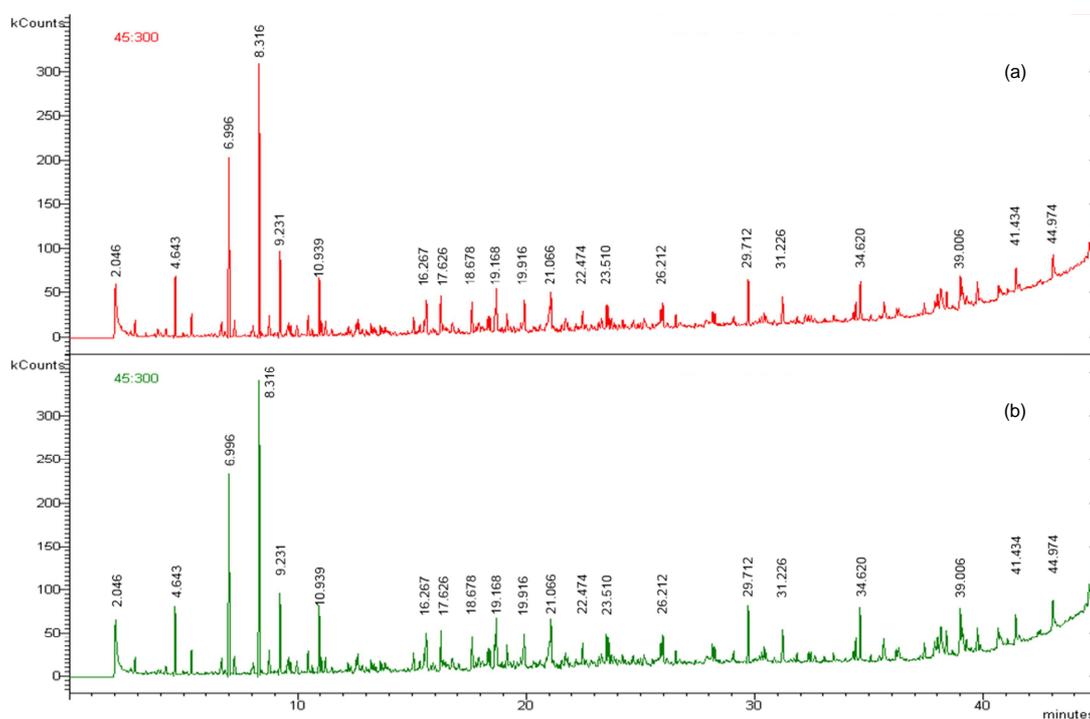


Figure 3. Gas Chromatograms of the pyrolysis oils (a. before accelerated aging; b. after accelerated aging)

FTIR identification results are presented in Figure 4. The black and blue spectra curves represent the abundance of the unaged and aged pyrolysis oils, respectively. It is observed that the abundance peaks are consistent for the unaged and aged intermediate pyrolysis oil at various wave lengths. This proves that the pyrolysis oil is stable in terms of the chemical functional groups, including the Alkyl (methylene) group (at 2926 cm^{-1} , 2853 cm^{-1} and 1492 cm^{-1}), esters and lactones (at 1729 cm^{-1}), nitro compounds with N-O band (at 1402 cm^{-1}), and some C-H band alkene functional groups (at 826 cm^{-1}). The minor variation seen in the spectra is attributed to the variation in the thickness of the sample. Thus the FTIR results indicate that the accelerated aging test did not cause any noticeable chemical changes in the intermediate pyrolysis oil, which validates the observation from the GC analysis in Figure 3.

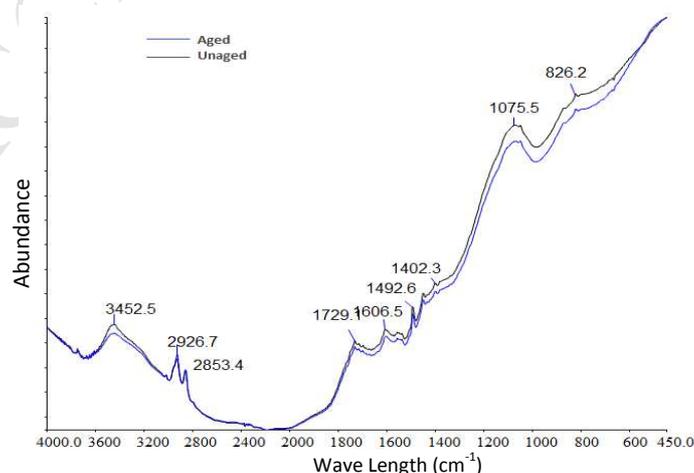


Figure 4. FTIR spectra of the pyrolysis oils before and after accelerated aging test

3.2.2. Physicochemical characteristics

Table 2 presents the physical and chemical characteristics of the pyrolysis oil. It is notable that, where the aged oil elemental analysis was not conducted as it has been demonstrated by the GC and FTIR results, that the elemental analysis for the unaged oil, show no obvious changes before and after ageing of the oil. The elemental analysis shows that the pyrolysis oils contain over 30% oxygen, which exists in the form of water and oxygen contained chemicals such as, phenolic compounds and aliphatic acid, ketone and esters. The water content is considerable (25.4%), and this value is after the separation of majority water from organics as an aqueous fraction product. Although aging conditioning did not cause chemical composition change in the pyrolysis oil, the water content has been significantly reduced to 14.8%. This raise concerns over the further phase separation of the pyrolysis oil during the long term storage and other characteristics changes.

Table 2. Characterisation of the pyrolysis oil

	Measure	Value
Elemental Analysis ¹⁾		
C	wt.%	57.4%
H	wt.%	9.4%
N	wt.%	2.1%
S	wt.%	0.5%
O ²⁾	wt.%	30.6%
Water content (before aging)	wt.%	25.4%
Water content (after aging)	wt.%	14.8%
Density (20°C)	g ml ⁻¹	0.972
HHV	MJ kg ⁻¹	28.0
Solids content ³⁾ (before aging)	wt.%	19.3%
Solids content ³⁾ (after aging)	wt.%	13.2%

¹⁾ Presented in ash free basis

²⁾ Calculated by difference

³⁾ Solids size >1µm

The solids content in the oil before and after aging was analysed. This is due to the fact that the GC and FTIR analysis could not reflect the changes in the solid content resulting from the oil aging. It was found that the solids content (>1µm) of the pyrolysis oil is measured as high as 19.3% before aging. However, after aging, this value was reduced to 13.2%. Potentially, there are two sources that can contribute to the solids content in the pyrolysis oil, including:

- 1) Char and ash particles from the feedstock. When the vapour is produced during pyrolysis, fine char and ash particles flowed with the hot vapour to the downstream process. In the present pyrolysis system, there is no hot-gas filter candle or cyclone to remove the particles before the condensation. Hence a large proportion of the char and ash particles were cooled with the condensate and ended up in the pyrolysis liquid.
- 2) Heavy organics formed during the pyrolysis and vapour condensation. These heavy viscous organics are produced from the pyrolysis of the plastics and lignin in the OFMSW feedstock, which tended to agglomerate when condensed and form semisolid agglomerates (>1µm) that were immiscible in an organic solvent in ambient conditions.

It is noted that during the accelerated aging (heating) of the pyrolysis oil, the char and ash particles do not change, e.g. dissolve or decompose. However, the heavy organics formed semisolid agglomerates that dissolve and/or decompose due to the accelerated aging. In fact, the stimulated Brownian motion of suspending materials in the oil can cause the breakdown of the semisolid agglomerates into smaller particles, leading to the reduction of solids content after aging in Table 2. Furthermore, the high solids content is unfavourable in the oil, because the solids are impurities that can affect the oil's physicochemical characteristics, such as combustibility and flow behaviour. The viscosity of the pyrolysis oil was found to decrease after aging in the below sections, which is believed attributed to the reduction of the solids content in the pyrolysis oil during the aging.

3.3 Effect of temperature and shear rate on viscosity of OFMSW pyrolysis oil

Figure 5 shows the measured dynamic viscosity for the OFMSW pyrolysis liquid at different temperatures and shear rates. It is observed that the OFMSW pyrolysis liquid's viscosity decreases with an increasing temperature following a nonlinear relationship in a semi-logarithmic coordinate. The nonlinear effect of the temperature on the viscosity was found to be the same at different shear rates. The viscosity decreases as strain rate increases at a constant temperature, which demonstrates that the OFMSW pyrolysis liquid is a non-Newtonian fluid.

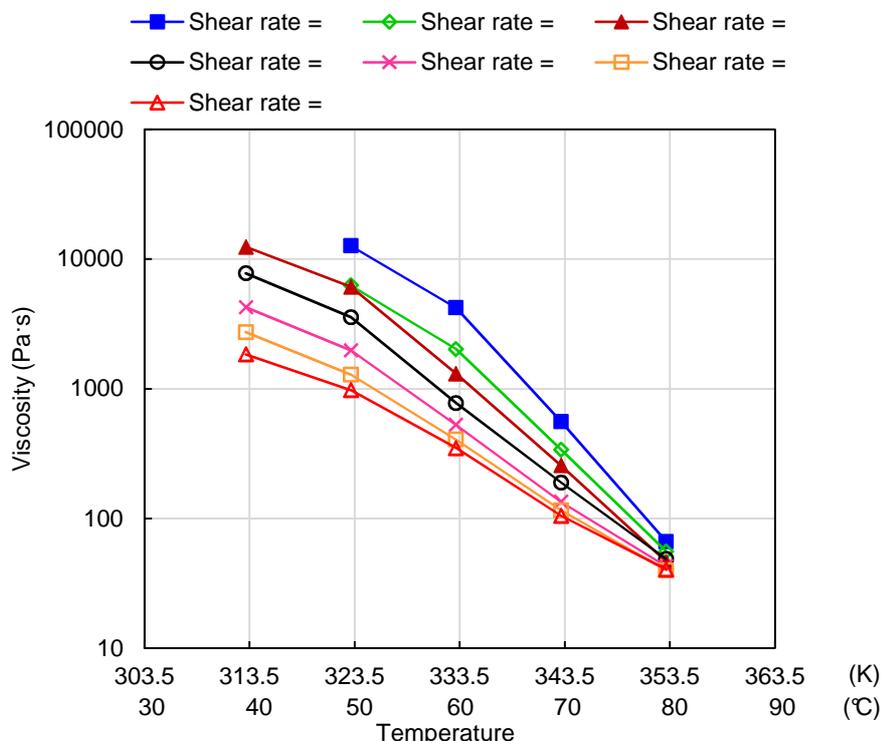


Figure 5. Viscosity of OFMSW pyrolysis liquid at different temperatures and shear rates (s^{-1})

Both Arrhenius and WLF temperature dependent viscosity models were employed to quantify the effect of temperatures on the viscosity of the OFMSW pyrolysis oil. Figure 6 shows the model predictions of the viscosity at a shear rate of $1 \text{ (s}^{-1}\text{)}$ and different temperatures when the Arrhenius and WLF models were used. It is found that the Arrhenius model predictions formed a linear curve at the semi-logarithmic coordinate with a coefficient of determination (R^2) of -20.03. A negative R^2 indicates that the Arrhenius model is not suitable for characterising the temperature dependence of the viscosity of the OFMSW pyrolysis oil. The WLF model-predicted viscosity shows a nonlinear relationship with the temperature with an R^2 of 0.9615. Thus it can be concluded that the WLF model is more suitable and can be used to quantify the temperature dependence of the viscosity for the OFMSW intermediate pyrolysis oil.

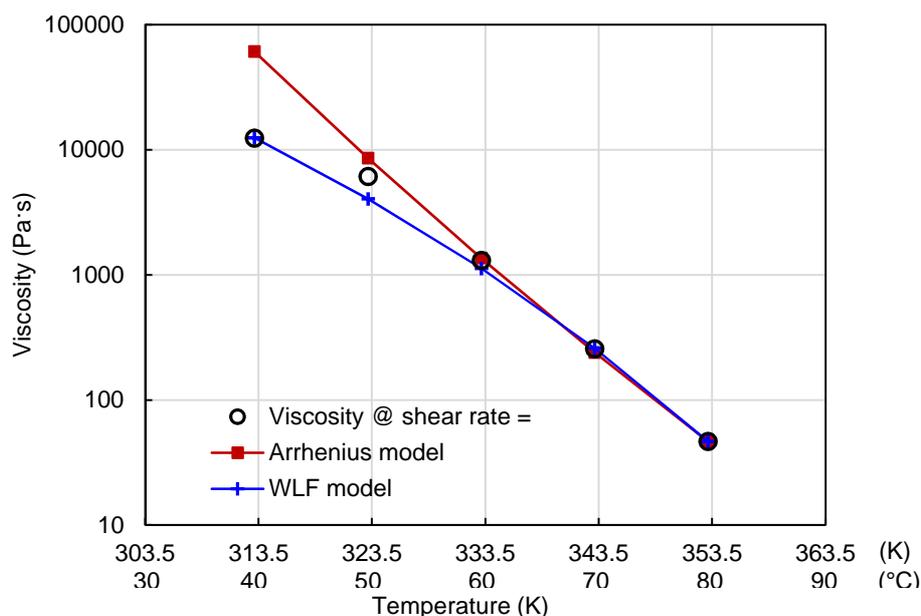


Figure 6. Measured viscosity at different temperatures (shear rate is $1, \text{s}^{-1}$) and model predictions by Arrhenius model ($R^2=0.203$) and WLF models ($R^2=0.9615$) for OFMSW pyrolysis oil

The above temperature dependent conclusion was found valid for the viscosity at all tested shear rates. Table 3 shows the determined parameters of the WLF temperature model and their R^2 values for the viscosity measured at different shear rates. It is found that R^2 values are all close to 1, thus it can be concluded that the WLF model can capture the temperature dependence of the viscosity at different shear rates. In addition, Table 3 shows that the $C2/C1$ value increases with an increasing shear rate. Since a higher $C2/C1$ value indicates a lower temperature dependence, this concludes that the viscosity's temperature dependence of the OFMSW pyrolysis liquid becomes less at a higher shear rate.

Table 3 Coefficients and R^2 values of WLF viscosity temperature model at different shear rates

Shear rates (s^{-1})	WLF Model Parameters			$C2/C1$	R^2
	C1	C2	$\eta_0(\text{Pa}\cdot\text{s})$		
0.2	-13	-122	41024	9.3	0.9878
0.5	-18.4	-164.4	20894.3	8.9	0.9935
1	-17.0	-161.6	12431.6	9.5	0.9615
2	-24.0	-230.0	7769.9	9.6	0.9789
5	-22.8	-238.2	4255.9	10.4	0.9865
10	-21.3	-241.4	2734.6	11.3	0.9924
20	-18.8	-236.6	1843.2	12.6	0.9867

3.4 Effect of Ageing on the Viscosity of OFMSW pyrolysis oil

Figure 7 shows the results of the dynamic viscosity for the unaged and aged pyrolysis oil at temperatures of 40, 50, 60, 70 and 80°C. Some of the viscosity results for accelerated aging samples were neglected (e.g. those at low shear rates and high temperatures) due to the device's limitations, the torque percent decreased to less than 10% of its capacity at 70°C and low shear rates, which also indicates that the viscosity at these conditions is very small for the aged pyrolysis oil. In general, Figure 7 clearly indicates a significant decrease in viscosity after aging of the OFMSW intermediate pyrolysis oil. However, there was no change in the chemical elemental composition after ageing, as demonstrated by the Gas Chromatograph and FTIR results in Section 3.2.1, which suggests that the viscosity drop was a result from a physical process. Table 2 has shown that the solids contents drop from 19.3% to 13.2% after aging, which can cause the reduction in viscosity. Fundamentally, this is

due to that the solid compounds (such as the heavy organic semisolid agglomerates) in the pyrolysis oil were decomposed into smaller particles, which reduced the shear-frictional forces (torque) and led to a decrease in viscosity of the OFMSW intermediate pyrolysis oil.

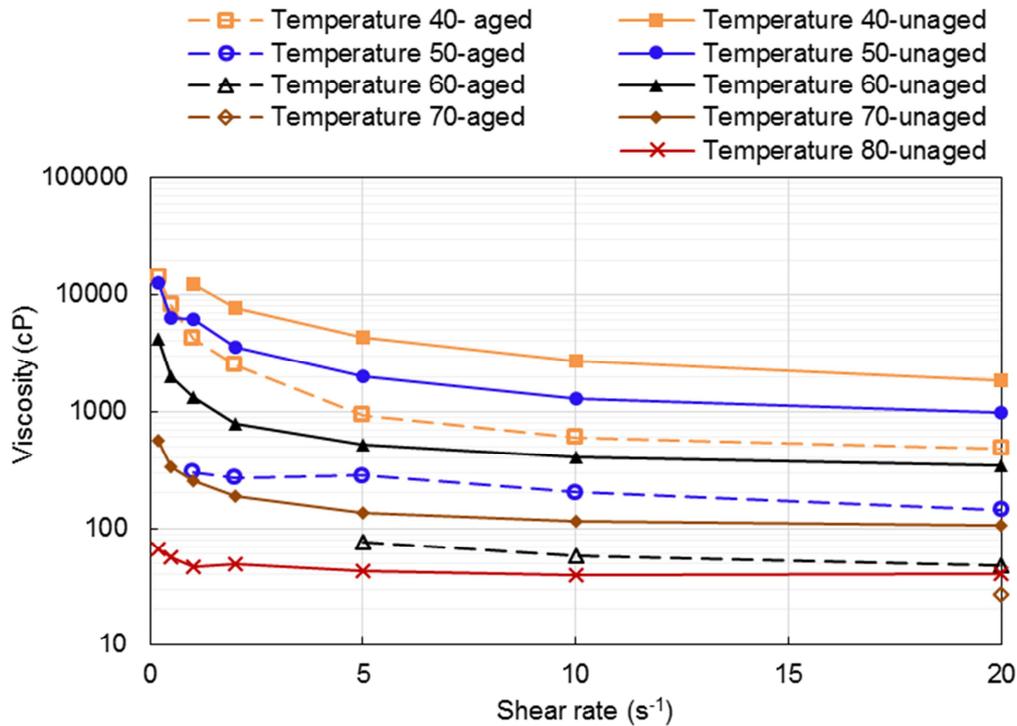


Figure 7. Viscosity vs. shear rates at different temperatures (°C) for unaged and accelerated aged pyrolysis oil

3.5 Viscosity master curve of OFMSW pyrolysis oil

Figure 8 replots the viscosity data with respect to shear rates at each of the testing temperatures. This clearly demonstrates the declining viscosity with the shear rate at a constant temperature. The Carreau model can be used to quantify the shear rate dependence of the viscosity of the pyrolysis oil. However the viscosity can only be measured at limited shear rates (e.g. at seven or fewer shear rates) at each temperature. This limitation was caused by the extended testing time when the shear rate is relatively low or by the restricted equipment torque resolution when the shear rate is high. The limited viscosity data under several shear rates and at one temperature may lead to an unreliable determination of the four parameters in the Carreau model (i.e. η_{∞} , η_0 , λ and n). To obtain a viscosity master curve, which is a viscosity spectrum over a wide range of shear rate (e.g., from extremely low to very high shear rates), a superposition method is proposed between the temperature and the shear rate. This shear rate-temperature superposition hypothesizes that the effect of the temperature change from T to T_0 on the viscosity is equivalent to the effect of the shear rate change from a shear rate $\dot{\gamma}$ to a new shear rate $\alpha_T \dot{\gamma}$ at the constant temperature of T , where α_T is a shift factor that is solely a function of temperature. In other words,

$$\eta(\dot{\gamma}, T) = \eta(\alpha_T \dot{\gamma}, T_0) \quad (7)$$

where α_T is the shear rate-temperature shift factor. In Section 3.3, the temperature dependent viscosity is characterised by the WLF model in Equation (5), and the results in Figures 5 and 6 prove that the temperature dependency of the viscosity for the OFMSW pyrolysis liquid can be modelled by the WLF function. Thus a WLF function based shear rate-temperature shift factor model is employed in below Equation (8). However, it is noted that the WLF function coefficients for the shear rate-temperature shift factor in Equation (8) are different from that for the temperature dependent viscosity in Table 3, which is for the model in Equation (5).

$$\alpha_T(T) = e^{-\frac{c_1(T-T_0)}{c_2+(T-T_0)}} \quad (8)$$

In this study, a reference temperature of 60°C was selected to construct the viscosity master curve. The viscosity data at temperatures greater than 60°C (e.g., 70 and 80°C) were horizontally shifted along the shear rate axis to the right via multiplying the shear rate by a shift factor α_T which is greater than 1. The viscosity data at temperatures less than 60°C (e.g., 40 and 50°C) was horizontally shifted along the shear rate axis to the left via multiplying the shear rate by a shift factor α_T which is less than 1. The shift factors were determined by shifting the viscosity data at temperatures other than the reference temperature to achieve a smooth viscosity curve (i.e. to ensure the superposition between the shifted viscosity and the viscosity at the reference temperature). Then, the viscosity at the reference temperature (60°C) and the viscosity shifted from other temperatures (i.e., 40°C, 50°C, 70°C and 80°C) to form a continuously smooth curve, as shown in Figure 8, which are the raw data for constructing the viscosity master curve at the reference temperature (60°C).

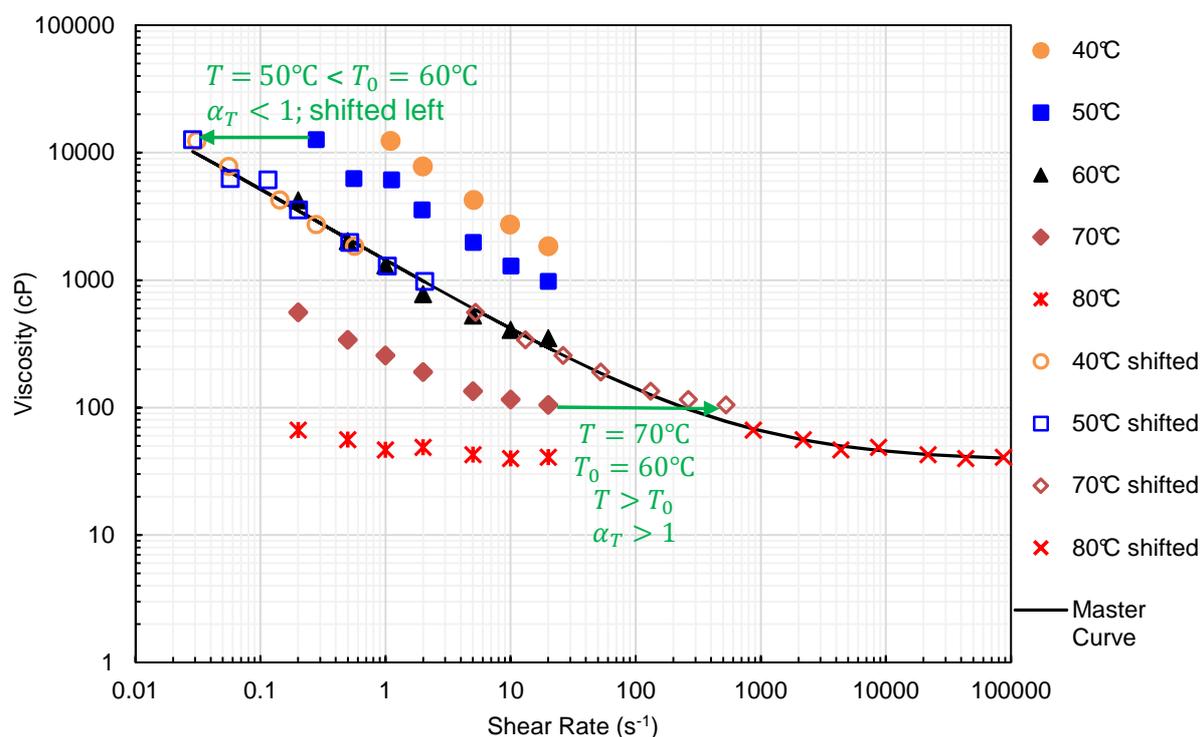


Figure 8. Viscosity vs. shear rates at different temperatures and viscosity master curve for the OFMSW intermediate pyrolysis oil modelled by Carreau Model ($R^2=0.955$)

Figure 9 shows the obtained shear rate-temperature shift factors for the viscosity at different test temperatures. It is found that the shift factor increases with temperature and is greater than 1 when the temperature is higher than the reference temperature. This indicates that a viscosity reduction due to an increased temperature can also be achieved by increasing the shear rate. The shift factors were modelled by the WLF function and it was derived that $\alpha_T = \exp\left(-\frac{14.9(T-60)}{-55.5+(T-60)}\right)$ with a coefficient of determination (R^2) of 0.9999. The high R^2 for WLF function demonstrates that the WLF function can capture the temperature effect on the shift factor and be used to predict the shear rate-temperature shift factor for the viscosity of the OFMSW intermediate pyrolysis oil.

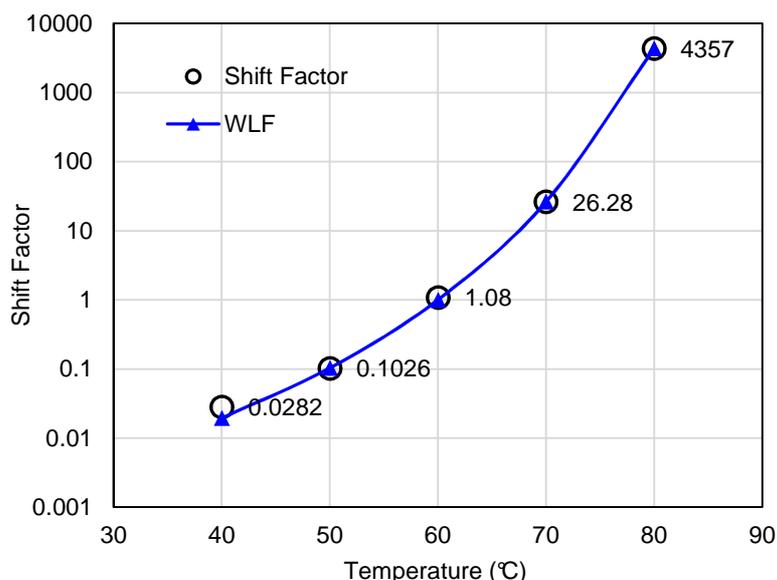


Figure 9. Shear rate-temperature shift factors and the predictions by WLF model ($R^2=0.9999$) for OFMSW pyrolysis oil

The shifted viscosity data and the viscosity data at the reference temperature in Figure 8 were utilized to formulate the viscosity master curve of the OFMSW pyrolysis oil. Based on these data, the Carreau viscosity model was formulated as below:

$$\eta = 38 + \frac{19164 - 38}{[1 + (100\dot{\gamma})^2]^{0.284}} \quad R^2 = 0.955 \quad (9)$$

The black and solid curve in Figure 8 shows the Carreau model predictions of the viscosity for the OFMSW pyrolysis liquid. The high R^2 (0.955 for the Carreau model) indicates that the Carreau master curve model is capable of capturing the viscosity characteristics at a wide range of shear rates. The viscosity master curve is a useful tool for viscosity predictions. Once constructed, the viscosity master curve can be used together with the temperature dependent shift factor (Equations 7 and 8) to predict the viscosity of pyrolysis oil at any specific shear rates or temperatures that may be out of the testing conditions. However, the temperature dependent viscosity model (e.g., WLF model in Equation 5) is still being used to investigate the effects of temperature on the viscosity. This is more straightforward and intuitive compared to the master curve, which is an indirect and indicative illustration of the temperature effect on viscosity.

Compared to the pyrolysis oils processed from fast pyrolysis of biomass materials (e.g., wood, grass, and sugarcane), which show relatively low viscosity and Newtonian fluid properties [5], the OFMSW pyrolysis liquid exhibits a much higher viscosity and non-Newtonian fluid characteristics. Thus the OFMSW pyrolysis liquid may not be suitable for the use as a fuel oil. A potential application of the OFMSW pyrolysis liquid is to substitute the light fraction (e.g., saturates or oils) of the bitumen which is a binder in asphalt used for road surface construction. The reduction of viscosity for the OFMSW intermediate pyrolysis oils after aging also enable the use of this pyrolysis oil as a softener for aged bitumen. This means that the increased viscosity of bitumen due to aging can be compensated by the reduced viscosity of the pyrolysis liquid after aging. OFMSW pyrolysis liquid has strong potential as a viable solution to the aging of the transport infrastructure including asphalt roads or highway surfaces.

4. Conclusions

- The organic fracture of municipal solid waste (OFMSW) feedstock has been successfully processed in an intermediate pyrolysis system. With a processing temperature of 500°C and a solid residence time of 1.5 minutes, the process mass balance includes pyrolysis oil (liquid organic fraction) 10.6%, liquid aqueous fraction 4.1%, permanent gas 23.2%, char 51.7%. The mass balance closure is 89.5%.

- The accelerated aging condition (80°C for 24 hours) did not result in any obvious changes in chemical composition to the OFMSW derived intermediate pyrolysis oil according to GC and FTIR analyses, but the solids and water content were considerably reduced.
- The dynamic viscosity of OFMSW pyrolysis oil decreases with temperature and its temperature dependence can be characterised by WLF model. OFMSW pyrolysis oil is a non-Newtonian fluid and its viscosity decreases with shear rate.
- Accelerated aging caused the reduction in the dynamic viscosity of the OFMSW intermediate pyrolysis oil, which resulted from the decomposition of the semisolid organic agglomerates in the solids content during the aging.
- Shear rate-temperature superposition method was proposed to create the viscosity master curve for the OFMSW pyrolysis oil and the WLF function can model the shear rate-temperature shift factor. The viscosity master curve is characterised by Carreau model, which can be employed to predict the viscosity of the OFMSW pyrolysis liquid at a specific temperature or shear rate.
- The relatively high viscosity and reduced viscosity after aging of the OFMSW pyrolysis oil has indicated its potential for application as a substitute of the light fraction in the bitumen for road construction.

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