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Intensification of Co-pyrolysis of Plastic with Biomass via Pretreatment

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Abstract

Biomass pyrolysis performance is improved through co-pyrolysis with hydrogen rich plastic producing more liquid fuel products of higher quality. Furthermore, beyond the synergetic effect, in catalytic pyrolysis the presence of plastic may facilitate the contact between catalyst and biomass. In this study, the effect of pretreatment of plastic/biomass was investigated, in order to further improve the above aims. The first pretreatment method was pre-degradation treatment at relatively low temperatures where solid state reactions alter the structure of plastic/biomass but no volatile products are formed. In addition, a second pretreatment method was used for the catalytic pyrolysis of cellulose, namely co-pressing of cellulose and catalyst particles into mixed pellets.

Thermogravimetric results confirmed that pre-degradation treatment reduced the decomposition temperature of cellulose. Pre-degradation diminished the hindering effect of the cellulose-derived char/ catalyst-coke demonstrating significant interaction between cellulose and lldPE (linear low density polyethylene) before the charring/coking stage of cellulose. While in the absence of catalyst, there is a minimal interaction between lldPE and cellulose, as the molten lldPE layers around cellulose particles inhibited the escape of the biomass-derived volatile products, the use of catalyst along with pre-degradation provided maximum interaction between lldPE and cellulose pyrolysates which proceeded at lower reaction temperature without any hindrance from char/coke formation. Furthermore, pre-degradation treatment increased the liquid yield with associated increase in char/coke yield. The presence of lldPE during the cellulose pyrolysis decreased the concentration of char/coke on the catalyst while higher amounts of hard coke/char had accumulated on the pre-treated samples. Liquid product characterisation indicated that co-pressing of cellulose with catalyst is more effective in converting cellulose-derived products into aromatics.

The results suggest that pre-treatment processes have increased the synergy between lldPE and cellulose, thereby enhancing the quantity and quality of the desired liquid product.

Keywords: Pre-treatment process, Co-pyrolysis, Liquid characterisation, Coke characterisation

1. Introduction

Renewable energy has become the focus of most recent research due to their vast availability, zero pollutants emission and their potential application as a liquid fuel (Bridgwater and Peacocke, 2000). Biomass is the only renewable energy source that yields solid, gaseous and liquid fuels similar to the products obtained from fossil fuels processing (Bridgwater and Peacocke, 2000; Fekhar et al., 2020), they can be used as a cheap source for energy generation and synthesis of high value-added chemicals (Soysa et al., 2015; Praveen Kumar and Srinivas, 2019). Bio-oil from thermal degradation of biomass typically contains 45–50 wt% oxygen (Praveen Kumar and Srinivas, 2019). The presence of oxygen makes it behave differently from hydrocarbon fuels (Mohan et al., 2006) due to the low heating value, high acidity, corrosiveness, and high viscosity, which collectively make the bio-oil unstable (Kabir and Hameed, 2017). Therefore, upgrading of bio-oil is necessary in order to compete and replace petroleum fuels. Over the past decades, research were focused on the use of catalysts for upgrading the bio-oil from biomass (Bridgwater and Peacocke, 2000; Fekhar et al., 2020; Soysa et al., 2015; Praveen Kumar and Srinivas, 2019; Mohan et al., 2006; Kabir and Hameed, 2017; Zhang et al., 2015; Li et al., 2013; Chen et al., 2015; Lee et al., 2016). However, poor hydrocarbon yields and high char/coke formation are the major drawbacks for this process (Zhang et al., 2015; Li et al., 2013). To address these issues different method of biomass pre-treatment have been developed and most noticeable route was torrefaction method (Chen et al., 2015). Torrefaction is a thermal pre-treatment of biomass in which the raw biomass is

heated in an inert atmosphere between 200–300 °C for the purpose of upgrading solid biomass fuel (Chen et al., 2015; Lee et al., 2016; Lee et al., 2018). Studies suggested that torrefied biomass was easily decomposed into small oxygenates, such as furans, which are the main intermediates for the formation of aromatic hydrocarbons over acid catalysts (Lee et al., 2016; Lee et al., 2018; Kim et al., 2017a). The shortcoming with torrefaction is the formation of large amount of char/coke compared to the raw cellulose due to the increased charring and crosslinking of cellulose during torrefaction (Chen et al., 2015; Lee et al., 2016; Lee et al., 2018; Kim et al., 2017a).

The relative abundance of hydrogen (H/C_{eff}) in a feedstock determines the detriment of charring/coking process (Zhang et al., 2015). Feedstocks with H/C_{eff} less than one are difficult to convert to hydrocarbons by zeolites due to rapid catalyst deactivation by char/coke deposits (Zhang et al., 2015; Li et al., 2013). Generally, char/coke yield increases with decreasing effective hydrogen index (H/C_{eff}) of the feedstock and since biomass is hydrogen-deficient ($H/C_{eff} \sim 0.3$), it results in a low hydrocarbon yield (Li et al., 2014). The hydrogen-deficient environment also leads to rapid char/coke formation, which eventually deactivates the catalyst (Li et al., 2014; Zhang et al., 2014). The rapid deactivation of catalyst caused by char/coke reduces the lifetime of the catalyst and the need for frequent catalyst regeneration could make the process impractical (Xue et al., 2016a). To further improve the quality of the bio-oil and minimize the char/coke formation, a hydrogen rich co-reactant is introduced in the process along with the lignocellulosic biomass (Li et al., 2013; Alam et al., 2020). Studies have experimented the co-feeding of biomass with alcohols such as methanol and butanol, which have high H/C_{eff} ratios (Alam et al., 2020; Zhang et al., 2012). The results indicated that adding of alcohols enhanced the aromatic yield and decreased the char/coke yield from biomass catalytic pyrolysis (Zhang et al., 2012). Compared with alcohols, waste plastics represent a cheaper hydrogen source that is abundantly available. Plastics have high content of hydrogen,

for instance, polyethylene and polypropylene which are the most commonly used plastics have an effective hydrogen index ($H/C_{eff} = 2$) (Fekhar et al., 2020; Praveen Kumar and Srinivas, 2019; Kim et al., 2017a). Therefore, waste plastics could serve as a promising hydrogen sources when co-fed with hydrogen-deficient biomass. According to several studies, introducing a hydrogen rich waste plastic as a co-reactant in biomass co-pyrolysis increases the liquid yield (Al-Salem et al., 2018; Gunasee et al., 2017; Chen et al., 2016; Onal et al., 2014; Yang et al., 2016), enhanced the aromatics yields and lowers the coke formation (Miandad et al., 2016; Miandad et al., 2017; Muneer et al., 2019; Dorado et al., 2015; Nikbin et al., 2015; Lu et al., 2018). The synergy of co-feeding plastics with biomass increased the H/C ratio and modifies the reaction mechanism of oxygen removal by substituting decarbonylation and decarboxylation reactions with dehydration reaction (Al-Salem et al., 2018; Martinez et al., 2014). The mechanism of free radical interactions contributes to the synergistic effect in the co-pyrolysis process in producing the improved bio-fuels with higher heating value (Al-Salem et al., 2018; Martinez et al., 2014; Paradela et al., 2008).

The mechanism of non- catalytic co-pyrolysis of polymer and biomass, involved the formation of radicals from biomass decomposition which initiated the thermal scission of the polymer chain (Sharypov et al., 2002; Sharypov et al., 2003). Then the hydrogen transfer reactions between the polymer chain and biomass radicals stabilized the primary products formed from biomass thermal degradation (Sharypov et al., 2002; Ryu et al., 2020). In the presence of catalyst, the major transformation involved Diel-Alder reaction between the reaction intermediates such as furans and olefins into aromatic hydrocarbons (Ryu et al., 2020; Rezaei et al., 2017).

As stated before and shown by previous studies (Lee et al., 2016; Lee et al., 2018; Kim et al., 2017a; Li et al., 2014), the performance of biomass catalytic pyrolysis and co-pyrolysis can be enhanced through pre-treatment process. Therefore, this study examined a novel pre-treatment route using thermal pre-degradation and hydraulic pressing methods. The influence of these post-treatment methods in non-catalytic and catalytic co-

pyrolysis of lldPE and cellulose was studied and compared with the normal mixing without any pre-treatment. Cellulose and lldPE were selected because cellulose comprises the largest fraction of biomass while lldPE represents large amounts of waste plastics generated. We wanted to keep our initial study of co-pyrolysis of plastics with biomass relatively simple and avoid further complex issues. Although trends on interactions between the biomass constituents during pyrolysis emerge, the full picture is far from being established. In particular, we wanted to exclude effects from lignin, another biomass constituent which itself is a complex mixture of aromatic compounds. This way we were able to focus on possible synergies during plastic co-pyrolysis and its advantageous effects.

For this purpose, TGA analysis, reactor experiments and GC characterization were employed. In addition, the effects of lldPE content, catalyst type and reaction temperature were investigated to identify the appropriate experimental conditions on the product yields of the pre-treated samples.

2. Experimental

2.1 Materials

The polymer sample used is lldPE in pellet form (particle size 1-2 mm, density 0.928 g/cm³, average molar mass of 117 kg/mol provided by Vantage Polymers Ltd. The biomass model compound is α -cellulose purchased from Sigma-Aldrich Co., Ltd UK, in powder form with average particle size of 100 μ m. The catalysts used include HY and USY zeolites in powder form provided by Grace GmbH with an average particle size of 1 μ m and Montmorillonite (Aluminium Pillared Clay) purchased from Sigma-Aldrich Co., Ltd UK, with a particle size of 100 μ m. The detailed properties of the catalysts are stated in Table 1.

2.2 Experimental setup

The experimental rig as shown in Fig. 1 is made - up of a semi-batch pyrex reactor with two semi-circle infrared heating elements for fast heating connected to a temperature controller, mass flow controller and two condensers placed in ice baths for liquid collection. At the beginning of the experiment, the catalyst sample was dried under a nitrogen stream at 473 K for 30 min. Before the actual experiment, the reactor was purged with 100 mL_N/min of nitrogen for 15 min, determined by a mass flow controller (MFC) in order to remove any oxygen from the reactor. The Liquid sample was collected in the condenser. The gases including hydrocarbon products were collected in a gas bag and disposed of safely. For each experimental run, the reactor and furnace temperatures were measured and recorded by a thermocouple each. The initial amount of cellulose, lldPE and their co-feed is equal to 2g in all experiments. The feed to catalyst ratio was varied, by varying the amount of the catalyst. The experiment was usually run for 30 min. At the end of each experiment, the condenser was weighed to calculate the mass of the liquid collected and the reactor was cooled and weighed to determine the mass of the converted feed. At the end of the experiment, the majority of the feed had been converted to gasses and liquids, leaving in the reactor only catalyst with deposited coke/char.

For all the pyrolysis experiments a constant nitrogen flow rate of 10 mL_N/min was used. The amount of lldPE and catalyst were varied during co-pyrolysis experiments between 0.25 – 1.00 g while the reaction temperature was fixed at 723 K - 823 K.

2.3 Pre-treatment process

To improve the degradation behaviour of the co-mixing feed and enhance the quality of their product yield, different types of pre-treatment methods were employed in this research work which includes pre-degradation and co-pressing methods. This ensured that effective synergy occurs between the lldPE, cellulose and catalyst.

2.3.1 Normal mixing

Normal mixing involves mixing of the cellulose, lldPE and catalyst thoroughly using spatula. As shown in figure 2, normal mixing presented much similarity with thermal degradation due to the complex nature of biomass structure and the crystalline nature of cellulose. These necessitated the needs of pre-treatment prior to the primary pyrolysis.

2.3.2 Pre-degradation treatment

Pre-degradation involves heating of the mixture of lldPE and cellulose in the presence and absence of catalyst to a temperature of 423 K for 10 minutes, a temperature at which lldPE had melted and in presence of catalyst solid state polymer chain reactions had taken place but no volatile products formation (Manos et al., 2000). As the polymer has melted, the mixture was stirred constantly for about 1 min resulting in a uniform mixture of lldPE and cellulose. As shown in Fig. 2, this has provided intimate contact between the mixing reactants and the catalyst, thereby enhancing the catalyst activity.

2.3.3 Co-pressing

Besides pre-degradation treatment, the use of co-pressing was due to the fact that co-pressing was the only alternative method to bring about intimate contact between cellulose and catalyst. In co-pressing method, the mixture of cellulose, lldPE and catalyst were stirred thoroughly with a spatula as in a normal mixing. After this stage, the mixture was placed on a hydraulic press and pressed for 5 min at a weight of 3 tons for 5 times, so as to produce intimate contact between the cellulose, lldPE and catalyst. As shown in Fig. 2, pre-treatment using co-pressing and pre-

degradation produced higher clean oil and reactor, making the process less time consuming and economically viable compared to the thermal and normal mixing methods.

2.4 Experimental Calculations

Conversion to volatile products was the fraction of the initial mass of the feed (lIdPE, cellulose and co-mix), reacted to form the volatile products.

The percentage liquid yield is the mass of the liquid collected divided by the initial amount of the feed i.e. the fraction of the original feed converted to the liquid products multiplied by 100.

$$Y_l = m_l / m_f * 100$$

Where Y_l = Liquid yield, m_l = Mass of the liquid collected, m_f = Mass of the feed

The percentage coke/char yield is the mass of the coke/char obtained after the experiment divided by the initial amount of the feed and represents the fraction of the original feed converted to coke/char multiplied by 100.

$$Y_c = m_c / m_f * 100$$

Where Y_c =Coke/char yield, m_c = Mass of the coke/char obtained, m_f = Mass of the feed

The coke/char concentration is the amount of coke/char deposited on the catalyst divided by the catalyst mass and represents the amount of coke/char formed per g of catalyst. It is estimated by TGA and converted to yield based on the catalyst amount in the reactor.

$$C_c = m_c / m_{cat}$$

Where C_c = Coke/char concentration, m_c = Mass of the coke/char deposited on the catalyst, m_{cat} = Mass of the catalyst

2.5 Liquid sample analysis

The liquid products were analysed on a Shimadzu 2014 gas chromatograph equipped with a flame ionization detector (FID) using a non-polar Rtx-1 DHA 100m x 0.25mm x 0.50 μ m capillary column. The hydrogen flow rate was 30 mL_N/min and the injector temperature was set at 270 °C. The temperature program began with a hold at 40 °C for 10 min followed by a ramp of 5 °C/min to 270 °C, and a hold for another 30 min while the FID detector temperature was set at 300 °C. A calibration mixture of normal alkanes C₅ – C₂₀ (standard) was run at the beginning of the analysis to assign retention time to each components. The whole sample for analysis was divided into intervals between the boiling points of the normal alkanes of the calibration mixture. The mass fraction corresponding to each interval was calculated from the sum of the area fractions of all the components in this interval. The mass fraction of each component is set equal to the area fraction (Gobin and Manos, 2004; Akpanudoh et al., 2005; Gulab et al., 2010). To each interval, the probability density function value was then calculated, as being equal to the mass fraction of this interval divided by the temperature interval width ΔT . Hence the probability density function is expressed as %/K. In the graphs of the boiling point distribution, each interval was represented by its middle value. All components with retention time smaller than that of n-pentane were assigned to a group corresponding to the boiling point interval between n-butane and n-pentane (272.70-309.20 K). This was repeated for all 16 groups and a total distribution curve for the overall sample was constructed as shown in the Table 2.

2.6 Thermal gravimetric analysis

The TGA measurements were carried out with Perkin Elmer Pyris TGA instrument. In a typical run ca. 5-10 mg of the feed and catalyst were heated to 473 K at a rate of 10 K/min and was maintained for 30 min under nitrogen flow (30mL_N/min) to remove the adsorbed water and any reaction mixture components. After this period, in TGA experiments with the raw feed, the

sample was held at 873 K for 30 min to complete the degradation and then the temperature was ramped to 1073 K to remove any coke/char formed during the degradation process. Finally, the hard coke/char formed was removed by switching from nitrogen to air at the final temperature 1073 K.

For the coked/char catalyst sample, after the removal of the adsorbed water and reaction mixture components, the temperature was raised to 1073 K at a rate of 5 K/min and kept constant for 30 min at the final temperature. The hard coke/char deposited on the catalyst was burnt out by switching from nitrogen to air at the final temperature (1073 K).

2.6.1 Coke/Char Characterisation and Calculation

The coke/char characterisation is shown in Fig. 3. This method is simple and specific using the TGA of coked/char catalyst. It provides information about the character of coke components, more specifically their volatility.

As presented in figure 3 the procedure consists of removal of water and reaction mixture from room temperature to 473 K. The coke/char components were classified into soft coke/char and hard coke/char. The soft coke/char was removed from 473 K to 1073 K through volatilisation in inert nitrogen while the hard coke/char remains on the catalyst even at high temperature (1073 K) and was removed by burning i.e. by switching the atmosphere from nitrogen to air as demonstrated in Fig. 3. The coke components are predominantly from hydrocarbon transformation over acidic catalysts while the char mainly formed from thermal degradation of biomass components.

$$\text{Soft coke/char (\%)} = \frac{\text{Mass of soft coke/char}}{\text{Total mass of coke}} * 100$$

$$\text{Hard coke/char (\%)} = \frac{\text{Mass of hard coke/char}}{\text{Total mass of coke/char}} * 100$$

Where *Mass of soft coke/char* is the total weight of the coke/char removed in nitrogen atmosphere from 473 K to 1073 K and *Mass of hard coke/char* is the total weight of the coke/char removed in air atmosphere at the final temperature (1073 K) while *Total mass of coke/char* correspond to the total weight of soft and hard coke/char respectively.

3. Results and Discussion

3.1 Experimental results from TGA of lldPE, cellulose and their co-feed

TGA of lldPE, cellulose and their mixture were performed to examine the effect of pre-treatment (pre-degradation) in non-catalytic and catalytic pyrolysis as shown in Figs. 4 and 5 respectively.

As shown in Fig. 4, the thermal degradation of cellulose in the absence of catalyst took place within the range of 550 – 650 K, whereas lldPE decomposed at higher temperatures of 673–763 K. In contrast, the mixture of cellulose and lldPE (1:1) exhibited two stages of mass loss with 25.0% weight loss occurring at 573 – 650 K and the remaining weight loss taking place between 650 -773 K. This result indicates that thermal decomposition of cellulose in the co-pyrolysis has been delayed and lldPE in the mixture is not significantly affected by cellulose. When the catalyst was used as shown in Fig. 5, there are no significant changes in the degradation pattern of cellulose and it is co-pyrolysis with lldPE using the normal mixing, without any pre-treatment. The significant difference with the thermal degradation is the char/coke

deposited on the catalyst which was burnt out only at the final temperature of 1073 K. Catalytic degradation of cellulose with HY using normal mixing has 12.0% char/coke and this amount reduced to 6.0% when mixed with lldPE. A unique feature displayed by thermal co-pyrolysis of cellulose and lldPE is the hard coke/char of about 2.0% deposited during the process despite the thermal degradation of the individual components generating no hard coke/char as shown in Fig. 4. The results thus indicate that in the absence of catalyst, there is minimal interaction between cellulose and lldPE.

As shown in Fig. 5, when pre-degradation was used for co-pyrolysis, the degradation pattern has shifted completely to lower temperatures indicating higher interaction between cellulose and lldPE. The effect of this thermal pre-treatment method was shown outright by comparing the lldPE degradation using the normal mixing and pre-degradation respectively. As shown in Fig. 5, the co-pyrolysis of cellulose with lldPE using pre-degradation took place in three stages. The first stage occurred within the range of 520–620 K, corresponding to over 50.0% removed weight fraction. The second stage was up to 735 K corresponding to additional removal of more than 25.0% weight fraction while the last stage represents slow decomposition of thermally stable residues. This is a remarkable result as most of the weight removal took place below the degradation temperature of pure cellulose. The second stage of the co-pyrolysis was shifted to high temperatures as a result of catalyst deactivation influenced by char/coke deposited on the catalyst. This stage happens early when using the normal mixing, which has slightly increased the thermal stability of lldPE. The minor shift in the degradation temperature during the catalytic pyrolysis of cellulose with HY can be explained by the restricted catalytic reaction, which only occurs at the external surface of HY catalyst. The kinetic diameter of cellulose is much larger than the pores size of HY and therefore, it is difficult for cellulose to diffuse into the pores of HY catalyst. The few acid sites located on the external surface of HY zeolite participated in the

initial cracking of cellulose and the smaller cracked molecules diffused into the HY pores and underwent further conversion (Kim et al., 2016). Kim et al. (2016) carried out catalytic co-pyrolysis of lldPE and cellulose with HY catalyst. The result of the TGA from the co-pyrolysis had a shoulder at higher temperature, which was not detected during the pyrolysis of lldPE over HY. They suggested that the char formed during cellulose pyrolysis could cause solid-solid interactions with the lldPE and act as a thermal stabilizer for lldPE increasing its pyrolysis temperature. The delay in the thermal degradation of biomass incorporated into plastic as shown in Figs. 4 and 5 was observed in previous studies (Lee et al., 2018; Alam et al., 2020; Sharypov et al., 2002; Rezaei et al., 2017; Parparita et al., 2014; Park et al., 2018a; Park et al., 2018b; Kim et al., 2017b; Jeong et al., 2019; Xue et al., 2017). The softening of lldPE occurs at around 573 K, followed a plastic state which inhibits the release of volatiles from cellulose by the formation of a coating layer on the surface of cellulose. Rapid generation of volatiles from lldPE occurs upon further heating which ruptures the coating on cellulose composites and causes the weight to decrease quickly. The lldPE acts as a hydrogen donor during co-pyrolysis process (Kim et al., 2017a), which inhibits the recombination and cross linking reactions that increase char formation and therefore less amount of coke/char was formed from the co-pyrolysis compared to the individual catalytic pyrolysis of cellulose with HY zeolite as shown in Fig. 5. Using the pre-degradation method for the catalytic co-pyrolysis, HY catalyst produces larger amount of coke/char at temperatures lower than 673 K and emits larger amount of volatiles during the coke/char stabilisation at temperatures higher than 673 K (Li et al., 2013; Lee et al., 2016).

3.2 Pyrolysis reactor experiments

3.2.1 The effect of pre-treatment on the product yields

The prime objective of this study was to improve the quantity and quality of the product yields from catalytic co-pyrolysis of cellulose and lldPE with the aid of pre-treatment. As stated under

the methodology two types of pre-treatment were deployed i.e. co-pressing method and pre-degradation treatment. As for this section, co-pressing was applied only to catalytic pyrolysis of cellulose while catalytic pyrolysis of lldPE and its co-pyrolysis with cellulose were pre-treated using pre-degradation treatment. The results of the product yields are reported in Fig. 6.

Reproducibility experiments were carried out and based on the calculated experimental error range of these experiments, error bars are added in the figures (Appendix L).

Based on Fig. 6, 15.5% and 5.5% of liquid and coke yields are obtained from catalytic pyrolysis of lldPE using normal mixing. With pre-treatment (pre-degradation) the values change to 59.5% and 4.0% for the liquid and coke yields respectively. For cellulose catalytic pyrolysis without pre-treatment, 41.5% and 25.0% of liquid and char/coke yields are produced. Using pre-treatment (co-pressing method) the values increase to 52.0% and 26.0% respectively. Catalytic co-pyrolysis of cellulose and lldPE showed similar trend with cellulose. The liquid yield increases from 29.7% to 46.0% while the char/coke yield increased from 19.8% to 25.0% for normal and pre-treated (pre-degradation) samples respectively. Pre-degradation was very effective in increasing the liquid yield from catalytic pyrolysis of lldPE, considering the fact that, the lldPE sample used in this study was in particles form. Pre-degradation provided intimate contact between the lldPE and catalyst thereby allowing the reaction to be completed at lower temperature, avoiding extreme coke formation. The same principle works when pre-degradation/co-pressing was applied to cellulose and its co-pyrolysis with lldPE, thus enhancing the liquid yield. As shown in Appendix H for non-catalytic co-pyrolysis of lldPE with cellulose, the presence of lldPE increases the liquid yield and decreases the char/coke yield. The change in mechanism during catalytic pyrolysis and co-pyrolysis of cellulose resulted in higher coke/char formation. This mechanism was intensified with pre-treated samples resulting in high liquid and char/coke yields respectively. Pre-treatment has enhanced the activity of the catalyst because

of the proximity of the reactants to the acid sites. Similar results were reported by Lee et al. (2016) from catalytic co-pyrolysis of torrefied cellulose and polypropylene. Their results showed higher amount of aromatics and solid residues using pre-treated torrefied cellulose. Positive synergistic effects on the catalytic co-pyrolysis of biomass and plastic over larger pore catalysts have also been reported (Lee et al., 2016; Lee et al., 2018; Kim et al., 2017b). To further explore the influence of experimental parameters on the pre-treated samples, pyrolysis experiments were carried out and the results were presented in the next section.

3.2.2 Effect of the catalyst content and reaction temperature on the product yields of the pre-treated samples (co-pressing)

Catalyst plays a vital role in catalytic pyrolysis as the selectivity of product depends on the application of the right catalyst at the appropriate amount. The ratio of feedstock to catalyst is very important, because the addition of more catalyst above a specific amount may not increase the overall degradation rate, due to the added catalyst not being in contact with the feedstock. As shown in Fig. 7, the amount of the catalyst was varied between 0.25 - 1.00 g and the effect of the catalyst addition was studied at constant reaction temperature and N₂ flow rate.

As shown in Fig. 7 the liquid yield decreases and coke/char yield increases as the amount of USY catalyst increased from 0.25 - 1.00 g. The liquid yield decreases from 54.0% to 50.0% while the coke/char increases from 20.0% - 23.5%. As shown in Appendix I all the catalysts used have decreased the liquid yields and increased the char/coke yields compared to the thermal co-pyrolysis with the exception of HY zeolite which produced the highest liquid yield. USY has lowest liquid yield and the highest char/coke yield (Appendix I) because of it is larger pore size and strong acidity. When the amount of USY increased (Fig. 7), stronger acidic sites

are accessible by pyrolysis vapour, which then promotes the conversion of oxygenates pyrolysates into aromatic. The extra-framework aluminum in USY has also created mesoporous sites acting as a space for the growth of char/coke precursors, which resulted in more char/coke deposition on the catalyst (Lee et al., 2016; Lee et al., 2018; Kim et al., 2016; Liao et al., 2019). Fig. 8 shows the effect of increasing reaction temperature on the product yields of the pre-treated samples. The catalytic co-pyrolysis of cellulose and lldPE with USY was carried out at different reaction temperature of 723 K to 873 K. The results as shown in Fig. 8 indicated that, the liquid yields went through maxima as the temperature increased from 723 K to 873 K while the coke/char yields decreases steadily.

The liquid yield increases from 46.0% at 723 K to nearly 50.0% at 773 K, reaching a maxima of 55.0% at 823 K before decreasing to 36.0% at 873 K. The coke/char yield decreases from 25.0% at 723 K to 16.0% at 873 K. The liquid yield increased at the beginning, because of the spontaneous cracking of the carbon chain, decomposition, and devolatilisation of the pyrolysates and continues with increasing reaction temperature. At high temperature, the liquid yield decreased due to the secondary cracking reactions of the pyrolysis vapour that was converted to low-molecular-weight compounds and non-condensable gases. As the pyrolysis temperature increases, coke/char yield decreases due to products volatilisation prior to coke/char formation. Similar study by Hassan et al. (2019) reported that the bio-oil amount rose to a maximum as the temperature increased from 723 K to 773 K and leveled off as the temperature elevated to 973 K. Conversely, the solid residues decreased with increasing reaction temperature (Zhang et al., 2014; Kim et al., 2016; Sharypov et al., 2002; Hassan et al., 2019).

3.3 Liquid Product Characterisation. The effect of co-pressing on the boiling point distribution of the bio-oil constituents.

The liquid sample characterisation was carried out using a non-polar capillary column, which aids in the separation of the components of the liquid product mixture according to their volatility/boiling point. As it is impossible and impractical to identify the hundreds of individual chromatographic peaks, we present the liquid analysis results in the form of Boiling Point Distribution, according to the methodology described in Section 2.5 of the Experimental. Due to the complexity of the components samples, the results discussion would be based in three component groups, i.e. the lighter fraction, which includes the components in the boiling point range from 272.70 K to 424.00 K, the middle fraction, which includes the components in the boiling point range from 424.00 K to 526.70 K and the heavier fractions which include the components in the boiling point range from 526.70 K to 617.00 K.

This section compares the boiling distribution of the bio-oil produced from catalytic pyrolysis of lldPE, cellulose and their mixture using the normal mixing and co-pressing method. The results are presented in Fig. 9. Liquid produced by catalytic pyrolysis of lldPE contained a narrow boiling point distribution with a maximum within the lighter fraction. Cellulose compared to lldPE has a wide range of product distribution with a maximum around the heavier fraction. As shown in Appendix J, cellulose thermal cracking produces predominantly heavier fraction and levoglucosan as the major product of cellulose thermal cracking (Lee et al., 2016; Lee et al., 2018; Li et al., 2014; Park et al., 2018a; Kim et al., 2017b; Lee et al., 2020). In the presence of catalyst the oxygenates from thermal cracking of cellulose underwent a series of deoxygenation reactions, such as dehydration, decarbonylation, decarboxylation, and oligomerization to form aromatics at the acidic sites (Lee et al., 2020). This leads to the changes in the boiling point distribution with sudden increased in middle fraction (Fig. 9). With the pre-treated sample, the

boiling point distribution was predominantly in the middle fraction which signifies intensive catalytic activity when cellulose was hydraulically pressed with USY catalyst.

The co-pyrolysed sample showed similar boiling point distribution with the pre-treated cellulose but due to the presence of lldPE it contains more middle fraction at the expense of heavier fraction. Increasing the content of the catalyst in the co-pyrolysed sample increases slightly the middle fraction with the heavier fraction decreasing steadily. The catalyst content has little impact on the product distribution from the catalytic co-pyrolysis. Similar studies by Lee et al. (2016) and Lee et al. (2020) showed that the hydrocarbon yield increased while the oxygenated compounds decreased with the increase in catalyst-to-feedstock ratio. To further unveil the effect of lldPE content in the catalytic co-pyrolysis with cellulose, catalytic co-pyrolysis experiments were carried out with pre-treated (co-pressing method) samples containing different amounts of lldPE as shown in Fig. 10.

Unlike with USY catalyst (Fig. 9), the boiling point distribution from co-pyrolysis with HY catalyst showed different product selectivity favouring heavier fraction at the expense of lighter fraction. Individually, lldPE with HY consists mostly of lighter fraction while cellulose with HY showed a sharp decrease in the lighter fraction and increase in the medium and heavier boiling point fractions compared to the product from thermal cracking (Appendix J). The boiling point distribution of the product from catalytic co-pyrolysis showed further decrease in lighter fraction and increase in the medium and lighter fractions. Further addition of lldPE increases the medium fraction and decreases the heavier fraction. Even further addition of lldPE decreases the medium fraction and therefore 25.0% lldPE served as the maximum amount to enhance the middle range fraction in the catalytic co-pyrolysis of cellulose and lldPE (Figs. 9 and 10). As shown in Appendix J, 25.0% lldPE had produced the highest amount of heavier fraction in the absence of catalyst. More lldPE is needed to optimise the lighter fraction in the thermal co-

pyrolysis. In the presence of acidic catalysts (USY, HY) products from cellulose thermal cracking, primarily levoglucosan, are converted to furans via dehydration, while mono- and poly-aromatic hydrocarbons are formed via a series of reactions, such as cracking, deoxygenation (dehydration, decarboxylation, decarbonylation) and aromatization (Lee et al., 2016; Lee et al., 2018; Kim et al., 2017a). Furans can be converted to aromatics more efficiently when hydrogen-rich lldPE is co-fed with cellulose. The furans and olefins from cellulose and lldPE, can produce additional aromatic hydrocarbons via Diels-Alder reaction, which is the reaction between alkenes and dienes producing cyclic hydrocarbons (Li et al., 2013). The high amount of heavy boiling fraction with HY, could be explained by the relatively slower diffusion of levoglucosan into the pores of HY, due to the catalyst deactivation by coke/char formation (Kim et al., 2017a; Li et al., 2014). HY catalyst was reported to produce high amount of polycyclic aromatic hydrocarbon compared to monoaromatic hydrocarbons (Li et al., 2013; Lee et al., 2018; Park et al., 2018a). This could be another reason for the high amount of heavy boiling point fraction with HY (Fig. 10). The formation of large amounts of branched aromatic hydrocarbons is possible due to the higher surface area and larger cavities in HY structure (Lee et al., 2018). The production of mixed naphthalenes was suggested to come from the Diels–Alder condensation and dehydration of benzene and furan as well as the successive alkylation of toluene with intermediate allene (Xue et al., 2016b; Cheng et al., 2012). In a related work Park et al. (2018a) studied the catalytic co-pyrolysis of biomass and hdPE over HY catalyst. Findings from this study revealed higher selectivity to polycyclic aromatic hydrocarbons including tri-methyl benzenes, tetra-methyl benzenes, and alkyl naphthalenes. To amplify the influence of pre-treatment, an optimal reaction temperature is needed to improve the quality of the boiling point distribution. As shown in Appendix K higher reaction temperature of 873 K produced the maximum amount of the middle range fraction. Higher reaction temperature promoted the catalytic cracking of biomass and plastic producing large amounts of olefins and alkanes due to the suppression of alkylation reactions (Lee et al., 2020).

3.5 Coked/char catalyst characterization

TGA was used to quantify the amount of coke/char and to classify their components into soft and hard coke/char by considering different chemical character of the coke/char. Chen and Manos, (2004) and Wang and Manos, (2007) had used similar method to classify coke into coke precursors and hard coke. The results of this classification are presented in Table 3.

As presented in Table 3, lldPE coke components are predominantly hard coke, which are associated with coke deposited inside the pores of the catalyst. The volatility of lldPE pyrolysis coke components increased with pre-degradation and this can be beneficial in the regeneration of coked catalysts, as soft coke is removed easier. On the other hand cellulose produces predominantly soft char/coke. Thermal pyrolysis produced only char while in the presence of catalyst both char and coke are deposited on the catalyst. Coke is mostly formed from hydrocarbon conversion while char from the thermal decomposition of biomass-derived pyrolysates. Pressed cellulose with USY catalyst produced more hard coke compared to the normal mixing because of the intimate contact it provides between the cellulose and the catalyst which enhanced not only its pyrolysis but coke formation too. The same reason accounted for the higher percentage of hard coke in the co-pyrolysis of cellulose and lldPE using pre-degradation method. When the contact is intimate, deep conversion into aromatics can take place with subsequent deposition of hard coke on the catalyst. Similar results were also reported by Lee et al. (2016), Lee et al. (2018), and Kim et al. (2017b) who reported higher formation of aromatics and poly aromatics from torrefied cellulose compared to the raw cellulose. As shown in Table 3, cellulose contained higher concentration of coke/char, but this can be reduced through catalytic co-pyrolysis of cellulose with lldPE.

4. Conclusions

The main conclusions of this research are the following:

- Pre-treatment of lldPE and cellulose using pre-degradation treatment and co-pressing has allowed interactions to take place both in non-catalytic and catalytic co-pyrolysis.
- In the absence of catalyst, there is a minimal interaction between lldPE and cellulose, where the molten lldPE layers around cellulose particles inhibited the escape of the biomass-derived volatile products. The use of catalyst along with pre-degradation provided maximum interaction between lldPE and cellulose pyrolysates which proceeded at lower reaction temperature without any hindrance from the char/coke formation.
- The liquid yield trend showed that there is an optimal lldPE to cellulose ratio for higher liquid production.
- Higher catalyst content has increased the conversion of oxygenates pyrolysates into aromatic promoting growth of coke precursors, which resulted in more coke/char deposition on the catalyst. As the coke/char yield decreases with increasing temperature, the maximum liquid yield was obtained at 823 K. The lower liquid yield at high temperatures can be attributed to the secondary cracking reactions of the pyrolysis vapour that was converted to low molecular-weight compounds and non-condensable gases.
- The results of boiling point distribution showed that the presence of cellulose has promoted the chain scission of polyethylene to form the products with shorter carbon chains, thereby increasing the amount of medium boiling point fraction.
- The boiling point distribution using normal mixing contained predominantly heavier boiling point fraction while the pressed sample showed maxima at medium boiling point fraction. This indicated that co-pressing of sample is more effective in converting cellulose-derived products into aromatics and this pre-treatment can serve to improve the quantity and quality of the bio-oil from co-pyrolysis of biomass and plastic.

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Fig. 1. Schematic diagram of the laboratory semi-batch reactor system

Fig. 2. Schematic presentation of various pre-treatment methods

Fig. 3 . TGA of coked/char sample containing the description of coke/char characterisation

Fig. 4. TGA of non-catalytic degradation of lldPE, cellulose and their co-feed; mass fraction removed against temperature

Fig. 5. TGA of catalytic degradation of lldPE, cellulose and their co-feed using different pre-treatment method; mass fraction removed against temperature

Fig. 6. The liquid and coke/char yields for catalytic co-pyrolysis of cellulose and lldPE with USY catalyst using different pre-treatment method (cellulose 1.5g: lldPE 0.5g, catalyst 1.0g, reaction temperature

723 K, flow rate 10 mL/min). Pre-treatment method for cellulose catalytic pyrolysis: Co-pressing. Pre-treatment method for lldPE catalytic pyrolysis and its co-pyrolysis with cellulose: Pre-degradation treatment.

Fig. 7. The liquid and coke/char yields for catalytic co-pyrolysis of cellulose with lldPE at different USY catalyst content (cellulose 1.5g: lldPE 0.5g, pyrolysis temperature = 773 K, N_2 flow rate 10 mL/min)

Fig. 8. The liquid and coke/char yields for catalytic co-pyrolysis of cellulose with lldPE at different reaction temperature (cellulose 1.5g: lldPE 0.5g, catalyst 0.5g, flow rate 10 mL/min)

Fig. 9. Boiling point distribution from catalytic pyrolysis of lldPE, cellulose and their mixture with USY catalyst (pyrolysis temperature = 773 K, N_2 flow rate 10 mL_N/min)

Fig. 10. Boiling point distribution from catalytic pyrolysis of lldPE, cellulose and their mixtures with HY catalyst (pyrolysis temperature = 773 K, N_2 flow rate 10 mL_N/min)

Table 1 : Catalysts Properties

CATALYST	PROPERTIES				
	BET (M ² /g)	Micropore Volume (cm ³ /g)	Micropore Area (m ² /g)	External surface Area (m ² /g)	SiO ₂ /Al ₂ O ₃
HY	590.00 ± 23.50	0.26	532.40	72.58	2.5
USY	433.60 ± 14.08	0.19	361.02	72.58	5.7
Aluminium Pillared Clay	-	-	250.00	-	-

Table 2. Boiling point distribution intervals

Group of carbon atom	Boiling point (K)	Group of carbon atom	Average Boiling point (K)	$\Delta T(K)$	Retention time (min)
C ₄ H ₁₀	272.70	C ₄ H ₁₀ - C ₅ H ₁₂	290.95	36.50	-
C ₅ H ₁₂	309.20	C ₅ H ₁₂ - C ₆ H ₁₄	325.55	32.70	16.03
C ₆ H ₁₄	341.90	C ₆ H ₁₄ - C ₇ H ₁₆	356.75	29.70	20.94
C ₇ H ₁₆	371.60	C ₇ H ₁₆ - C ₈ H ₁₈	385.20	27.20	27.16
C ₈ H ₁₈	398.80	C ₈ H ₁₈ - C ₉ H ₂₀	411.40	25.20	33.26
C ₉ H ₂₀	424.00	C ₉ H ₂₀ - C ₁₀ H ₂₂	435.65	23.30	38.64
C ₁₀ H ₂₂	447.30	C ₁₀ H ₂₂ - C ₁₁ H ₂₄	458.20	21.80	43.37
C ₁₁ H ₂₄	469.10	C ₁₁ H ₂₄ - C ₁₂ H ₂₆	479.30	20.40	47.61
C ₁₂ H ₂₆	489.50	C ₁₂ H ₂₆ - C ₁₃ H ₂₈	499.05	19.10	51.49
C ₁₃ H ₂₈	508.60	C ₁₃ H ₂₈ - C ₁₄ H ₃₀	517.65	18.10	55.05
C ₁₄ H ₃₀	526.70	C ₁₄ H ₃₀ - C ₁₅ H ₃₂	535.25	17.10	58.51
C ₁₅ H ₃₂	543.80	C ₁₅ H ₃₂ - C ₁₆ H ₃₄	551.90	16.20	61.91
C ₁₆ H ₃₄	560.00	C ₁₆ H ₃₄ - C ₁₇ H ₃₆	567.60	15.20	65.26
C ₁₇ H ₃₆	575.20	C ₁₇ H ₃₆ - C ₁₈ H ₃₈	582.35	14.30	68.71
C ₁₈ H ₃₈	589.50	C ₁₈ H ₃₈ - C ₁₉ H ₄₀	596.30	13.60	72.43
C ₁₉ H ₄₀	603.10	C ₁₉ H ₄₀ - C ₂₀ H ₄₂	610.05	13.90	76.60
C ₂₀ H ₄₂	617.00	C ₂₀ H ₄₂ ⁺	617.00	-	81.45

Table 3. Coked/Char components classification

Coke/Char Classification				
Experiment type	% Soft Coke/Char	% Hard Coke/Char	Coke/Char Concentration	
IldPE + USY, Normal mixing	27	73	0.2.0	
IldPE + USY, Pre-degradation	40	60	0.24	
Cellulose, Thermal	72	28	-	
Cellulose + USY, Normal mixing	78	22	0.59	
Cellulose + USY, Pressed	71	29	0.51	
Cellulose + IldPE + USY, Normal mixing	68.3	31.7	0.35	
Cellulose + IldPE + USY, Pre-degradation	46.8	53.2	0.34	

Appendix A. GC raw data for thermal cracking of (i) lldPE, (ii) cellulose

Appendix B. GC raw data for catalytic cracking of cellulose with (i) HY, (ii) USY

Appendix C. GC raw data for (i) catalytic cracking of lldPE with USY, (ii) Cellulose + lldPE, thermal

Appendix D. GC raw data for catalytic co-pyrolysis of cellulose+ lldPE with (i) HY, (ii) USY

Appendix E. TGA raw data for catalytic cracking of cellulose + lldPE + HY zeolite

Appendix F. TGA raw data coke sample, cellulose + USY

Appendix G. TGA raw data coke sample, cellulose + IldPE USY

Appendix H. The liquid and coke/char yields for non-catalytic co-pyrolysis of cellulose with lldPE at different cellulose to lldPE mixing ratio (pyrolysis temperature = 823 K, N₂ flow rate 10 mL_N/min)

Appendix I. The liquid and coke/char yields for catalytic co-pyrolysis of cellulose with lldPE using different catalysts (cellulose 1.5g: lldPE 0.5g, catalyst 0.5g, pyrolysis temperature=773 K, flow rate 10 mL_N/min)

Appendix J. Boiling point distribution from thermal pyrolysis of lldPE, cellulose and their mixtures (pyrolysis temperature = 823 K, N₂ flow rate 10 mL_N/min)

Appendix K. Boiling point distribution from catalytic co-pyrolysis of cellulose and lldPE with USY catalyst

Appendix L. Raw data from reactor pyrolysis experiments

Replicates values										
Non-catalytic	Liquid yields					Coke/char yields				
Cellulose : IldPE (g)	1	2	3	Mean	SD	1	2	3	Mean	SD
2.0:0.0	54.00	55.00	50.00	53.00	2.60	19.50	19.00	20.00	19.50	0.50
0.0:2.00	63.00	65.00	61.00	63.00	2.00	2.90	3.00	3.10	3.00	0.10
1.75:0.25	62.00	64.00	66.00	64.00	2.00	17.80	18.00	18.20	18.00	0.20
1.50:0.50	56.00	52.00	54.00	54.00	2.00	16.00	15.50	16.50	16.00	0.50
1.25:0.75	52.00	54.00	50.00	52.00	2.00	13.50	14.00	14.50	14.00	0.50
1.00:1.00	44.00	43.00	42.00	43.00	1.00	16.40	16.00	15.60	16.00	0.40

Replicates values										
Catalytic	Liquid yields					Coke/char yields				
USY Content (g)	1	2	3	Mean	SD	1	2	3	Mean	SD
0.25	54.00	56.00	52.00	54.00	2.00	19.50	20.00	20.50	20.00	0.50
0.5	51.00	53.00	52.00	52.00	1.00	21.00	20.70	21.30	21.00	0.30
0.75	50.00	52.00	51.00	51.00	1.00	21.40	22.60	22.00	22.00	0.60
1	50.00	49.00	51.00	50.00	1.00	23.50	23.90	23.10	23.50	0.40

Replicates values

Catalytic	Liquid yields					Coke/char yields				
Catalysts type	1	2	3	Mean	SD	1	2	3	Mean	SD
Thermal	54.00	53.00	55.00	54.00	1.00	16.70	15.30	16.00	16.00	0.70
HY	57.00	55.00	59.00	57.00	2.00	19.80	20.00	20.20	20.00	0.20
APC	54.50	51.50	53.00	53.00	1.50	20.00	19.90	20.10	20.00	0.10
USY	53.00	51.00	52.00	52.00	1.00	21.00	20.00	22.00	21.00	1.00

Replicates values										
Catalytic	Liquid yields					Coke/char yields				
Temperature (K)	1	2	3	Mean	SD	1	2	3	Mean	SD
723	47.00	45.00	46.00	46.00	1.00	25.60	25.00	24.40	25.00	0.60
773	50.00	49.50	50.50	50.00	0.50	23.60	23.50	23.40	23.50	0.10
823	54.00	56.00	55.00	55.00	1.00	16.00	16.20	15.80	16.00	0.20
873	36.00	35.80	36.20	36.00	0.20	15.50	16.00	16.50	16.00	0.50

Replicates values										
Pre-treatment type	Liquid yields					Coke/char yields				
	1	2	3	Mean	SD	1	2	3	Mean	SD

lIdPE, Normal mixing	15.30	15.70	15.50	15.50	0.20	5.50	5.70	5.30	5.50	0.20
lIdPE, Pre-degradation	60.00	59.50	59.00	59.50	0.50	4.10	4.00	3.90	4.00	0.10
Cellulose, Normal mixing	41.00	42.00	41.50	41.50	0.50	25.00	26.00	24.00	25.00	1.00
Cellulose, Co-pressing	51.50	52.00	52.50	52.00	0.50	25.50	26.00	26.50	26.00	0.50
Cellulose: lIdPE, Normal mixing	29.70	29.30	30.10	29.70	0.40	19.80	20.00	19.60	19.80	0.20
Cellulose: lIdPE, Co-pressing	47.00	45.00	46.00	46.00	1.00	24.50	25.50	25.00	25.00	0.50