Homogenization of Heavy Tar and Plastics by Thermal Co-treatment to Prepare Liquid Fuel Feedstock

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Herein we focused on homogenization of heavy tar and three types of plastics (polyethylene (PE), polypropylene (PP), and polystyrene (PS)) by thermal co-treatment to prepare feedstock for liquid fuel production. The heterogeneous mixture was treated with different solvents at 300 °C for reaction times ranging from 0 to 3 h under N₂ atmosphere to produce liquefied feedstock. Pretreatment results for the different PS ratios indicated the carbon recovery values for the liquefied products. Further, the synergetic effects of the heavy tar and PS mixture significantly increased the concentrations of components such as ethylbenzene and (1-methylethyl)benzene. Moreover, thermal treatment of the heavy tar and plastic mixture with acetone resulted in ketone fractionation to form 4-methyl-4-penten-2-one and 4-methyl-3-penten-2-one. Additionally, the results indicated that the thermal co-treatment of heavy tar and other plastics (PE and PP) with various solvents generated less quantities of the liquefied product. Finally, the gas chromatography-mass spectrometry analysis indicated that reaction times did not significantly affect the product distributions of the liquefied product.

Key Words
Homogenization, Heavy tar upgrading, Thermal co-treatment

1. Introduction

Insoluble water tar or heavy tar is a by-product of biomass pyrolysis or gasification and comprises several useful compounds such as oxygenated carbon and aromatics which are generated during degradation and polymerization of biomass. Pyrolysis is the thermal conversion of oxygenated compounds in lignocellulosic materials into hydrocarbons and gaseous species (CO, CO₂) at temperature ranging from 200–700 °C, under inert gas atmosphere and in the total absence of oxygen. The heating value of tar is not high since its structure is characterized by several oxygen molecules. Therefore, the co-pyrolysis of biomass and carbonaceous materials could improve the heating values of the generated products and subsequently allow production of liquid fuel feedstock. Plastics are potential carbonaceous resources due to their high carbon and hydrogen contents. Presently, large quantities of plastics are utilized in the daily activities of human and are subsequently disposed by incineration. Nearly 358 million tons of plastic waste was generated from urban infrastructure industries, agriculture/forestry and construction activities in Japan in 201321). As indicated above, plastics can be utilized to increase the heating value of heavy tar. In addition, the degradation of plastics generates several beneficial compound such as aliphatic hydrocarbons, BTX, and PAH. Li et al. reported that co-feeding of cellulose with LDPE during catalytic fast pyrolysis with ZSM-5 catalyst produced high petroleum yields (52.1–55.6%C) and resulted in low coke formation. In addition, co-feeding of biomass with LDPE increased the concentrations of aromatic components in the condensable products.

Hassan et al. reported that the catalytic co-pyrolysis of terrified wood and polystyrene (PS) with HZSM-5 catalyst at 600 °C increased the concentration of aromatic hydrocarbons by more than 70%. Additionally, oxygenated compounds were primarily produced from the terrified wood while the production of major aromatic hydrocarbons, such as styrene, α-methylstyrene, 2-phenyl-1,2,3,4-tetrahydronaphthalene, diphenylpropane and diphenylbutane derivatives, could be attributed to the free radical reaction of the PS.
Lu et al. \cite{8} indicated that the co-pyrolysis of pine wood and plastics (polyethylene (PE) and polyvinylchloride (PVC)) improved the quality of the liquid products by decreasing the oxygen content of oil from 19.5–44.0% (PE) and 22.1–48.6% (PVC). Moreover, the degradation of PE released hydrogen radicals which further contributed to the degradation of pine wood.

Previous studies on co-pyrolysis have focused on physical mixing. Additionally, biomass and commodity plastics significantly differ with regard to several characteristics including pyrolysis temperature. Consequently, the pyrolytic products of biomass and plastics may not react efficiently. Furthermore, the oxygenated components of heavy tar inhibit the direct dissolution of plastics which are primarily composed of hydrocarbons. Moreover, the authors were unsuccessful in directly dissolving the commodity plastics in heavy tar. In this study, thermal co-treatment of heavy tar and commodity plastics was several solvent to prepare a homogenized feedstock for subsequent production of liquid fuel. Solvents act as intermediates and absorb degraded compounds during liquid formation. Sub/super critical solvents produce activated radicals which contribute to the depolymerization of biomass/polymers \cite{9, 10}. Furthermore, Cheng et al. \cite{12} and Miller et al. \cite{11} concluded that the application of organic solvents prevented the production of solid residue during pyrolysis of biomass in a batch reactor.

This study focused on determining the optimal pretreatment conditions for the co-pyrolysis of heavy tar, plastics, and solvents to obtain the homogenized liquid feedstock for subsequent production of liquid fuel. Therefore, heavy tar and various commodity plastic wastes (PE, polypropylene (PP), and PS) were treated under different conditions (i.e., different solvent types, ratios, and reaction times) at 300 °C. Finally, the homogenized feedstocks were compared to elucidate the reaction pathways and establish the optimal pretreatment conditions for homogenization.

2. Experimental

2.1 Materials

2.1.1 Heavy tar and plastic samples

The heavy tar sample was generated from the pyrolysis of pine wood pallets at 400 °C under steam atmosphere in a pilot scale fluidized bed reactor and subsequently collected by the water scrubber as a water insoluble fraction. Recycled pellets (1–3 cm) of PE and PP were obtained from the ECOS Factory (Tokyo, Japan). PS sample was obtained by fracturing food trays made of foam into fragments (1–3 cm). The elemental compositions of the samples are presented in Table 1.

2.1.2 Solvents

Analytical grades of all solvents (acetone 99.5%, tetrahydrofuran (THF) 99.5%, and n-hexane 96.0%) were obtained from the Wako Pure Chemical Industries, Ltd. (Saitama, Japan).

2.3 Homogenization by thermal co-treatment

Mixed samples (~ 2 g) and a solvent (20 ml) were mixed, stirred, and treated in an autoclave apparatus (Taiatsu Techno Corporation, Tokyo, Japan). Additionally, the reactor was purged with N2 gas (pressure = 0.4 MPa) and to remove oxygen before conducting the experiments. All of experiments were conducted at 300 °C and the reaction time ranged from 0 to 3 h. The reactor was cooled to room temperature by an electronic fan after the thermal treatment. The gaseous sample was collected in a gas bag and its composition was quantified by Agilent 300A Micro GC (INFICON, Yokohama, Japan) with two channels of column assemblies. A molecularsieve column (10 m × 320 µm × 12 µm) with a temperature of 100 °C and pressure of 30 psi was utilized for the quantification of H2, N2, CH4, and CO. The PLOT U column (8 m × 320 µm × 30 µm) was utilized for the analysis of CO2, C2H6, and C2H4 at the same temperature and pressure settings. Furthermore, Ar was the carrier gas for both the channels. The treated product was washed with 200 ml of fresh solvent and filtered by Whatman No.5 filter paper to separate the solid residue and the liquefied product. The solid residue was dried at 85 °C for more than 3 h. A mixture of the liquefied product and the solvent was obtained as the filtrate. The filtrate was

| Table 1 | The elemental analysis of heavy tar, polyethylene (PE), polypropylene (PP) and polystyrene (PS) |
|---------|-----------------------------------------------------------------------------------------------|
| Sample  | Ultimate analysis |
|         | C   | H   | N   | O   | H/C | O/C | HHV (MJ/kg) |
| Heavy tar | 70.6 | 8.8 | 0.0 | 20.7 | 0.8 | 0.5 | 328          |
| PE      | 82.3 | 18.2| 0.0 | 0.0  | 26  | 0.0 | 541          |
| PP      | 83.5 | 18.0| 0.0 | 0.0  | 26  | 0.0 | 539          |
| PS      | 92.5 | 78  | 0.0 | 0.0  | 10  | 0.0 | 425          |
evaporated in a vacuum rotary evaporator at 60 ℃ to purify the liquefied product. The composition of the liquefied products was determined by gas chromatography-mass spectrometry (Shimadzu GCMS-QP2010) and the capillary column was coated with Rtx-5MS (60 m × 0.25 mm i.d, 0.25 µm film thickness). The NIST database was utilized as the reference in this regard. The elemental compositions of the solid residue and the liquefied product were determined by the Macro Recorder JMA Auto Sample 1000 CHN analyzer (J-SCIENCE LAB Co. Ltd., Kyoto, Japan).

Carbon distributions of the solid and liquefied products were calculated from the experimental data as follows:

\[
\text{% carbon recovery} = \frac{C_{\text{product}}}{C_{\text{sample}} + x} \times 100
\]  

Where \(C_{\text{product}}\) is the amount of carbon in the solid residue, liquefied product or gaseous product (mol), \(C_{\text{sample}}\) is the amount of carbon in the substrate (mol), and \(x\) is the amount of carbon which reacted with acetone (mol).

The high heating value (HHV) of the liquefied product was estimated according to Friedl et al.\(^{13}\):

\[
\text{HHV} = (3.55C^2 - 232C - 2230H + 51.2C \times H + 131N + 20600) \times 10^{-3} \text{ (MJ/kg)}
\]

Where C, H, N, O is the amount of mass percent of element (carbon, hydrogen, nitrogen and oxygen).

3. Results and discussion

3.1 Homogenization of heavy tar and PS in acetone

In this study, homogenization of heavy tar and PS was conducted by thermal co-treatment. Heavy tar and PS mixture (with weight ratios ranging 1/0 to 0/1) were mixed with acetone for thermal treatment in a high pressure autoclave at a temperature of 300 ℃ for a duration of 3 h. Furthermore, the pressure was increased from atmospheric pressure to ~ 4.75 MPa when the experimental temperature reached 300 ℃. The distributions of carbon recovery in the solid, liquid and gaseous phase are presented in Fig. 1.

The amounts of liquefied yield was produced about ~ 84.0% when the PS content was equal to or lower than 25 wt% and decreased when the PS content was greater than 50 wt%. On the other hand, pure PS produced nearly 85% of the liquefied product during thermal treatment with acetone. Furthermore, the solid residue decreased while the gaseous and loss components increased at PS concentrations greater than 25%. The results showed that solid residue was easier produced from heavy tar than PS degradation. Light components might be lost during filtration and solvent evaporation. In fact, monobenzene (toluene, styrene and etc.) and light ketones were detected in the solvent recovered which the amounts were similar as the concentration in liquefied products (comparison by accumulated peak area of TIC, AN). Amount of gaseous products was calculated by calibration curve of external standard. However, gaseous products increased marginally (less than 1%) in this study.

The GC-MS analysis (Table 2) as well as the chemical fractionation (Fig. 2) of raw heavy tar and the liquefied products indicated that the major components of raw heavy tar were oxygenated aromatic compounds derived from the pyrolytic degradation of lignocellulosic materials. As indicated in Table 2, the thermal treatment of heavy tar with acetone increased the concentrations of light components, obviously oxygenated aromatic compounds in the liquefied products.

All of the compounds identified by GC-MS must be produced from heavy tar, PS and interactions of both reactions. Production mechanism of each compound can be, therefore, classified into three types such as (1) Individual production (IP); produced from heavy tar and PS without the interactions, (2) Synergetic production (SP); produced not only from heavy tar and PS but also from the interactions, (3) Synergetic degradation (SD); produced from heavy tar and PS but degraded by the interactions. By assuming that yield of each compound is proportional with initial amounts of substrates, superposing of TIC peak areas of each compound in pure heavy tar and pure PS mixture weighted by initial amounts of substrates can predict TIC peak area of each compound produced by individual production from heavy tar and PS mixture. In this paper, three peak areas of each compound in 25%, 50% and 75% mixture were compared with predicted one. When three measured areas of a compound are similar with predicted values within ±20% of predicted the compound is classified as individual production. A compound is classified to synergetic production when all three peak areas are above
Table 2 The products distribution of homogenization by thermal co-treatment of heavy tar and polystyrene: 300 °C for 3 h with acetone

| RT (min) | Identified products | Thermal co-treatment of heavy tar and PS mixture |
|----------|---------------------|-----------------------------------------------|
|          |                     | Heavy tar (%)                                 |
|          |                     | 0     15  25  50  75  100                     |
|          |                     | Area (%)                                      |
| 5.623    | Acetic acid         | 36    17  16  -  -  -                          |
| 6.667    | 2-Propanone, 1-hydroxy- | 25   -   -   -  -  -                           |
| 6.738    | Benzene             | 24    09  1.0  0.9  0.7  0.9                  |
| 8.776    | 4-Penten-2-one, 4-methyl- | -   24  2.4  1.9  1.0  -                       |
| 9.385    | Tolueno             | -     -   -   -  -  -                          |
| 10.341   | 3-Penten-2-one, 4-methyl- | -  104  96  8.3  5.0  24  14                   |
| 11.960   | 2-Pentanone, 4-hydroxy-4-methyl- | -   33  2.8  27  22  1.6  -                      |
| 12.944   | Ethylbenzene        | -     -   -   -  -  -                          |
| 14.313   | Styrene             | -     -   -   -  1.3  28  36  64  SD           |
| 15.816   | Benzene, (1-methylethyl)- | -   2.7  42  79  77  40  SP                  |
| 17.643   | 2-Furancarboxaldehyde, 5-methyl- | 26   -   -   -  -  -                           |
| 18.016   | Benzene, 1,2,3-trimethyl- | 1.7  1.3  1.1  -  -  -                          |
| 18.732   | alpha-Methylstyrene | -     -   -   -  1.5  35  52  77              |
| 20.846   | 2-Cyclopenten-1-one, 2-hydroxy-3-methyl- | 46   -   -   -  -  -                           |
| 22.149   | Phenol, 2-methyl-    | 3.0    16  -  -  -  -                          |
| 23.170   | Phenol, 3-methyl-    | 3.4    22  2.0  -  -  -                          |
| 24.105   | Phenol, 2-methoxy-   | 8.0    63  57  47  33  1.2  -  IP              |
| 29.319   | Phenol, 2-methoxy-4-methyl- | -   -   -   -  -  57  23  -                       |
| 29.375   | 2-Methoxy-5-methylphenol | 15.5  11.0 10.2  8.9  -  -                     |
| 33.383   | Phenol, 4-ethyl-2-methoxy- | 12.5  94  8.0  7.2  48  22  2  IP              |
| 33.749   | 1,2-Benzenediol, 4-methyl- | -   1.6  -   -  -  -                          |
| 36.576   | 2-Pentanone, 5-phenyl- | -     -   -   -  1.3  28  29  12           |
| 36.968   | Phenol, 2-methoxy-3-(2-proplyl)- | 46   -   -   -  -  -                           |
| 37.401   | Phenol, 2-methoxy-4-propyl- | 47   10.1 9.0  7.0  42  1.3  -  IP              |
| 38.087   | Benzenethanol, beta-methyl-acetate | -   -   -   -  -  22  -                        |
| 38.917   | Benzaldehyde, 3-hydroxy-4-methoxy- | 25   -   -   -  -  -                           |
| 39.230   | Phenol, 2-methoxy-4-(1-propenyl), (Z) | 3.8  -   -   -  -  -                        |
| 39.533   | 1,4-Methanoazulene, decahydro-4,8,8-trimethyl-9-methylene- | 30   -   -   -  -  -                           |
| 41.030   | Phenol, 2-methoxy-4-(1-propenyl)-(E) | 8.5  -   -   -  -  -                          |
| 42.640   | Ethanone, 1-(4-hydroxy-3-methoxyphenyl) | 2.9  -   -   -  -  -                          |
| 44.428   | Biphenylyl          | -     -   -   -  -  17  SD                      |
| 44.427   | 2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)- | 2.9  -   -   -  -  -                          |
| 45.534   | Benzene, 1,1'-methyl-1,2-ethanediylibis- | -   -   -   -  -  -                        |
| 49.321   | Benzene, 1,1'-propanediylbis- | -   6.8  11.5 16.3  18.2  18.6  SP             |
| 50.434   | Benzene, 1,1'-methyl-3,3-propanediylbis- | -   -   -   -  2.3  56  10.3  11.5           |
| 51.582   | (E)-Stilbene       | -     -   -   -  -  -                          |
| 52.397   | 1,2-Diphenycyclopropane | -   -   -   -  2.3  46  62  SD                   |
| 53.168   | Benzene, 1,1'-butanediylbis- | -  -   -   -  1.2  16  26  SD                       |
| 54.062   | Pentane, 1,4-diphenyl- | -     -   -   -  -  -                          |
| 55.06    | Anthracene, 9-ethenyl- | -     -   -   -  -  -                          |
| 60.864   | 2-Phenylglycerol     | -     -   -   -  1.8  22  SD                      |
| 60.990   | 4b,8-Dimethyl-2-isopropylphenanthrene, 4b,5,6,7,8,8a,9,9,10-octahydro- | 4.4  4.1  3.8  21  -  -  IP                  |
| 62.239   | 1-Phenanthrene-carboxaldehyde, 1,2,3,4,4a,9,10,10a-octahydro-1a-acetyl-1a-methyl-7-(1-methylthyl)-, [1S-(1.alpha.,4a.beta.)- | 5.0  5.1  4.2  20  -  -  IP                  |
| 63.269   | Phenanthrene, 2,5-dimethyl- | -   17  20  19  15  -  -  SP                    |
| 64.700   | 10,18-Bisnorbenz[a]a,11,13-pentacene | -  -   -   -  2.3  20  -  -  SD                        |
| 64.919   | 9-HCyclopenta(j)phenanthrene, 2,3-dihydro- | -  -   -   -  -  -  -  |
| 64.941   | 4H-Benz[a]anthracene, 5,6-dihydro- | -     -   -   -  22  13  SD                      |
| 66.275   | m-Terphenyl         | -     -   -   -  26  -  -                          |
| 66.574   | 1-Methyl-1,3-dimethylbenzene | -  -   -   -  2.6  20  -  -  SD                  |
| 67.518   | p-Terphenyl         | -     -   -   -  -  -                          |
| 68.464   | 2-Isopropyl-10-methylphenanthrene | -  12.4  -  13.3  84  -  -  |
| 68.451   | Phenanthrene, 1-methyl-7-(1-methylthyl)- | 46  -  12.5  -  -  -  39  -  |
| 71.279   | 8-Isopropyl-1,3-dimethylbenzanthrene | -  22  22  24  11  -  -  |
| 71.764   | 1-Phenanthrene-carboxylic acid, 1,2,3,4a,9,10,10a-octahydro-1a-acetyl-1a-methyl-ester, [1R-(1.alpha.,4a.beta.)- | 4.5  76  70  51  23  -  -  |
| 79.552   | 1,3,4,7-Terphenyl, 4-phenyl- | -     -   -   -  10  68  73  SD                  |
| 80.997   | 1,3,4,7-Terphenyl, 5-phenyl- | -     -   -   -  18  47  83  SD                  |
| 86.573   | 1,3,4,7-Terphenyl, 6-phenyl- | -     -   -   -  18  47  83  SD                  |
the predicted values and biggest difference exceeds 20% or to synergetic degradation when all three peak areas are below the predicted values and the lowest peak area is below 80% of the prediction. Some compounds which have a large variation with mixing ratio cannot be applicable to the three conditions to be indicated as unknown. Typical behaviors of individual production, synergetic production and synergetic degradation compounds are shown in Fig. 3 (a) and (b). Dashed lines on the figures are predicted peak areas.

Fig. 3 (a) indicates the cases of synergetic production, in which the TIC peak area (A Ni) of [a-1] ethylbenzene, [a-2] 1-methylethylbenzene, and [a-3] 1,1”-(1,3-propanediyl)bis- benzene significantly increased when the co-feed of heavy tar and PS was treated together. As shown in Table 2, fractions of Benzene and 2,5-dimethyl-phenanthrene are mainly attributed to synergetic production compounds. On the other hand, Fig. 3 (b) indicates [b-1] 5’-phenyl-1,1’:3,1”-terphenyl and [b-2] styrene as a case of synergetic degradation compounds. Synergetic degradation compounds are mainly allocated in fractions of 1,2-diphenylcyclopropane and 4’-phenyl-1,2’:1”-terphenyl while individual production compounds in fractions of 2-methoxyphenol (Table 2).

The individual and interacted reactions could be attributed to the following two reasons: (1) Heavy tar and acetone functioned as hydrogen and alkyl-donor during the thermal co-treatment. Subsequently, the hydrogen and alkyl radicals reacted with the degraded components of the PS to increase the formation of monobenzene. Obviously, the formation of PAHs in pure PS treatment such as 4’-phenyl 1,1’:2,1"-terphenyl and 5’-phenyl-1,1’:2,1”-terphenyl were decreased significantly by thermal co-treatment. In addition, styrene monomer can also reform into monobenzene by hydrogenation and alkylation. As report of Uzumkesici et al. 14), showed that ethylbenzene was the primary component of the liquid product generated during the co-processing of coal and PS at 500–600 °C since degradation of coal increased hydrogen radicals which reacted with the styrene monomer to produce ethylbenzene. (2) The degradation of heavy tar increased the concentrations of intermediate aromatic components in the system which reacted with the PS degraded components. Additionally, the production of light components was likely controlled by the substrates in the system. Wahyudino et al. 15) reported that stabilization of radicals produced during tar degradation could be achieved by the addition of hydrogen from a donor solvent. In addition, the solvent could react with the products of biomass degradation to produce light components in the liquid products.

Table 3 presents the carbon concentrations before and after the homogenization of heavy tar and PS by

![Fig. 2 Chemical fractionation of liquefied products via thermal treatment of heavy tar and PS mixture by GC-MS analysis: 300 °C for 3 h with acetone](image)

![Fig. 3 Synergetic effect of homogenization by thermal co-treatment of heavy tar and PS mixture: a) Increasable products, b) Decreasing products: 300 °C for 3 h with acetone](image)
thermal co-treatment. The concentrations of the liquefied products were predicted by superposing the concentrations of the products generated during the thermal treatment of pure heavy tar and PS. The comparison of predicted and observed carbon concentrations indicated that increasing PS ratios in the substrate increased the carbon concentrations. Furthermore, the thermal treatment of pure PS indicated a carbon content of 94.0% in the liquefied product which could be attributed to the removal of hydrogen radicals. Additionally, the carbon content of the liquefied product increased from 70.6 to 78.1% during treatment of pure heavy tar and could be attributed to deoxygenation of the lignocellulosic derivatives. Moreover, carbon concentrations reported from the experimental results were higher than the predicted values for all treatment conditions. Therefore, the synergetic effects between the degradation products of heavy tar and PS increased the hydrocarbon concentration (Fig. 3).

The relationships between the atomic ratios of H/C and O/C in the liquefied products before and after the thermal treatment were explained by the Van Krevenlen diagram (Fig. 4). The atomic ratios of pure or mixed substrates were based on the proportions of heavy tar and PS in the substrate. The results indicated that oxygen content reduced with increasing PS ratios. The O/C and H/C atomic ratios ranged from 0.0 to 0.20 and 1.0 to 1.50, respectively. After the thermal co-treatment, O/C ratios ranged from 0.0 to 0.12 while H/C ratios from 1.10 to 1.20. The decreasing O/C and H/C ratios suggested that the structure of heavy tar disintegrated by deoxygenation and dehydrogenation to form gaseous species (CO and CO2) and water. The treatment of pure PS indicated that the H/C ratio decreased slightly while the O/C value did not change. Furthermore, the reaction with acetone resulted in ketone fractionation in the liquefied product. The results indicated that the interaction between the PS degraded compounds of PS and acetone had not so much. The thermal co-treatment results indicated that the O/C ratio obtained from the experiment deviated from the predicted value when the PS concentration in the substrate was less than 50%. Furthermore, this deviation was significant for the 25%PS mixture. Therefore, the co-feeding of heavy tar and PS synergistically increased the production of hydrocarbons.

Table 3 Carbon content in mixture substrate and liquefied products treated with acetone solvent at 300°C for 3 h

| Sample     | Carbon content (%wt) | Substrate | Thermal co-treatment | Experiment | Prediction |
|------------|----------------------|-----------|----------------------|------------|------------|
| Heavy tar  | 70.6                 | 78.1      | -                    |            |            |
| 15%PS      | 73.9                 | 81.3      | 80.5                 |            |            |
| 25%PS      | 76.1                 | 83.7      | 82.1                 |            |            |
| 50%PS      | 81.5                 | 85.8      | 86.1                 |            |            |
| 75%PS      | 87.0                 | 90.5      | 90.1                 |            |            |
| PS         | 92.5                 | 94.0      | -                    |            |            |

Fig. 4 The relationship of atomic ratios by Van Krevenlen diagram of liquefied products via thermal co-treatment at various PS mixture ratios: 300°C for 3 h with acetone

Fig. 5 High heating value (HHV) of liquefied products by thermal co-treatment of heavy tar and PS mixture: 300°C for 3 h with acetone
of the 25%PS mixture indicated the highest increase in the experimental value about 3.1% in comparison to the predicted value.

The reaction pathways for homogenization by thermal co-treatment are presented in Fig. 6. The degradation of heavy tar and PS during the thermal co-treatment process produced intermediate components such as derivatives, PS fragments and free radicals H', OH, CH3' and others. Additionally, acetone was also activated to produce free radicals. Trikoupis et al. 30 reported that the formation of the acetone radical could occur from CH3C(=O)CH3' or other intermediates. Fragments formed during the degradation of heavy tar and PS reacted with the acetone radicals to initiate ketone fractionation through pathways No. (1). In general, the production of 4-methyl-3-penten-2-one (mesityl oxide), 4-methyl-4-penten-2-one (isomesityl oxide) and 4-hydroxy-4-methyl-2-pentanone (diacetone alcohol) were produced by aldol condensation and dehydration of acetone. 22 - 24. The production of those components from several substrates including pure acetone was summarized in Fig. 7. Those components were slightly produced from pure acetone and decreased while PS ratio increased. Possibly, the formation of those compounds can be promoted by mixing with heavy tar. In addition, those compounds can generate from other carbonyl and hydroxyl group in heavy tar fractions.

For instance, 1-hydroxy-2-propanone can be reacted by acetone. Aldol condensation and dehydration of acetone and other components (ketones and alcohols) were reported by Ordóñez et al. 25 and Novodárszki et al. 26 which the results showed the chemical production from the reaction of acetone. Moreover, acetone can react with PS monomer to form 5-phenyl-2-pentanone.

Reactions such as depolymerization and isomerization likely occurred during in pathway No. (2). The thermal production of those components from several substrates including pure acetone was summarized in Fig. 7. Those components were slightly produced from pure acetone and decreased while PS ratio increased. Possibly, the formation of those compounds can be promoted by mixing with heavy tar. In addition, those compounds can generate from other carbonyl and hydroxyl group in heavy tar fractions.

![Fig. 6 Reaction pathways of homogenization by thermal treatment of heavy tar and PS: 300 °C for 3 h with acetone](image-url)

![Fig. 7 Comparison the production of ketones fractionation in liquefied products by accumulated peak area of TIC chromatogram: 300 °C for 3 h with acetone](image-url)
co-treatment of heavy tar and PS primarily generated aromatic components and a few aliphatic. The formation of oxygenated aromatic compounds during the degradation of heavy tar attributed to the presence of oxygen molecules in the heavy tar structure. The composition of heavy tar was determined by the GC-MS (Table 2) and the results indicated the presence of several oxygenated aromatic compounds. The synergetic effects of homogenization resulting from the thermal co-treatment PS could be attributed to pathway No. (3). The results indicated that the concentrations of SP chemicals such as ethylbenzene, (1-methylethyl)benzene and 1,1'-(1,3-propanediyl)bis-benzene significantly increased while that SD chemicals such as 5'-phenyl-1,1'3,1'-terphenyl decreased (Table 2).

The synergetic effects of the co-treatment inhibited the polymerization of PS by free radicals produced during the cracking of heavy tar to subsequently increase the concentrations of small aromatic components in the liquefied product. In addition, the active radicals of acetone enhanced the degradation of heavy tar and plastics by reacting with the substrates to disintegrate their structures. Additionally, deoxygenation of heavy tar produced CO2 and H2O. Polymerization of degraded compounds can produce the solid residue. The results indicated that the optimal PS concentration was 25% and could be applied to other conditions in this study.

### 3.2 Effect of different solvents and plastics on homogenization

In this study, the effects of different solvents on the homogenization of the 25% of PS mixture were determined. The effects of acetone, THF, and hexane were observed at 300 °C for duration of 3 h under N2 atmosphere. The operation pressures for no solvent, acetone, THF, and hexane were 0.8, 4.75, 4.5 and 3.0 MPa, respectively. The treated products were washed with 200 ml of acetone and evaporated at 60 °C in vacuum to obtain the liquefied products. The carbon recovery values of the homogenized products have been presented in Fig. 8.

Liquefied products obtained by thermal co-treatment with the THF indicated the highest carbon recovery (93.7%) and the lowest solid residue production (6.2%). The carbon recovery values due to acetone and hexane were 84.1 and 78.6%, respectively. Thermal co-treatment without solvent indicated the lowest carbon recovery (67.5%) and high solid residue formation (27.0%). The compositions of the liquefied products were determined by the GC-MS analysis. The liquefied products were primarily characterized by oxygenated compounds regardless of the solvents type. The results indicated that 4-methyl-3-penten-2-one was only produced during the interaction with acetone. The addition of the solvents increased the degradation of the substrates into liquefied products by preventing the formation of solid residue (Fig. 8). The availability of the solvents for homogenization followed the order THF>acetone>hexane.

Homogenization treatments with different solvents and plastics were also carried out. Before the experiments, the influence of reaction time (0 to 3 h) on homogenization was confirmed for the 25%PS mixture with THF as the solvent. The results obtained that reaction time had slightly affected to increase in the carbon recovery by solid from 0.8% at 0 h (heating up from room temperature to 300 °C and cooling down) to 6.2% at 3 h. Since high liquid production was targeted in this study and a temperature history at the initial heating up stage was unstable, homogenization products with holding time for 30 min with different solvents and plastics were compared. Substrates containing 25 wt% of plastic were prepared by mixing heavy tar with three types of plastics, i.e., PE, PP and PS. The prepared substrates were treated with acetone, THF, and hexane at 300 °C for 30 min under N2 atmosphere. The obtained products were analysed by the same procedure. The tests for dissolution of heavy tar and plastics were conducted for all solvents at room temperature. Heavy tar and PS mixture indicated higher solubility in THF than acetone and was insoluble in hexane. PE and PP did not dissolve in any solvent. The carbon recovery values of the products obtained after thermal co-treatment are presented in Fig. 9. The results indicated that gaseous products constituted less than 1% and primarily comprised CO2 species. The highest liquid production was observed for the PS containing substrate with value of 90.8%, 97.4% and 80.2% for acetone, THF, and Hexane, respectively.

The carbon recovery values for the solid residue of the 25%PS mixture were 9.1% (acetone), 2.6% (THF), and
Thermal co-treatment with PE and PP indicated lower production of the liquefied with significantly high yields of the solid residue for all solvent. Additionally, the non-degraded compounds were limited and no degraded compounds were observed in the solid residue. The effects of solvents were similar to those as mentioned above (homogenization of 25%PS at 300 °C for 3 h). The production of liquefied products by the solvents followed the order: THF > acetone > hexane. The conversion of PE and PP into liquefied products increased to 50.8 and 65.1%, respectively, due to thermal co-treatment with THF. Thermal co-treatment with hexane exhibited the highest solid residue production, i.e., 59.3% (PE), 56.4% (PP) and 19.7% (PS). It is likely that hexane did not form active fractionation groups (such as hydroxyls and ketones) which are characterized by the lone pairs of electron oxygen. Hence, hexane indicated fewer active radicals than the other solvents. Furthermore, aromatic components obtained from the degradation of heavy tar readily accumulated to form the solid residue.

The application of PS generated more aromatic compounds in the system; however, the quantity of solid residues produced was less than that generated by PE and PP. These results could be attributed to the synergistic effects of heavy tar and PS which increased the electron transfer between the degraded substrates to generate small chemicals in the liquefied product. Previous studies have reported low-temperature degradation and high liquid production during co-treatment with PS in comparison to with PE and PP. Demirbas et al. 17), Aguado et al. 18) and Hassan et al. 7) concluded that the thermal degradation of plastics (PE, PP, and PS) occurred at temperature greater than 350 °C, and the highest liquid yields were observed for PS treatment. The TGA results reported by Miandad et al. 19) indicated that the degradation of PS was initiated at 400 °C. Further, pyrolysis at 450 °C for 75 min resulted the highest concentration of the liquid product (80.8 wt%).

Table 4 presents the product distributions of the liquefied products as identified by the GC-MS analysis. The different compositions were identified depending on types of plastics and solvents. The results for the chemical fractionation of the liquefied products are summarized in Fig. 10. These results were obtained from the TIC chromatograms and corresponded to the peak accumulation area of chemical fraction. The percentage of chemical fractionation was compared to the total peak area of the identified compounds. The results indicated that phenol and phenol derivatives were the primary chemical fractions while hydrocarbons represented a minor component.

Several aromatic compounds were indicated in the liquefied products of all plastics. The degradation of PE and PP did not increase the production of aliphatic compounds; however, an increase in the production of cyclic, phenols and phenol derivative was observed. Li et al. 6), reported that catalytic pyrolysis at 550 °C resulted in aromatization of 28.3 and 35.4% of the LDPE and PP, respectively. In this study, aromatization of PE and PP could be attributed to reaction with the OH- radicals (generated from heavy tar degradation). The aromatized PE and PP further produced phenol and phenol derivatives. Thermal co-treatment of heavy tar and PS increased the proportion of hydrocarbons under all experimental conditions. Additionally, the results indicated that the total quantity of hydrocarbons generated during a reaction time of 3 h (Fig. 2) was less than the quantity of phenols (and its derivatives) generated during a reaction time of 30 min (Fig. 10). Therefore, deoxygenation
Table 4 The products distribution of homogenization by thermal co-treatment of heavy tar and plastics (PE, PP and PS) at 300 °C for 30 min with different solvents

| RT (min) | Identified products                      | Acetone | THF | Hexane |
|---------|-----------------------------------------|---------|-----|--------|
|         |                                         | PE      | PP  | PS     |
| 5.673   | Acetic acid                             | 27      | 19  | -      |
| 6.176   | Furan, tetrahydro-                      | -       | -   | -      |
| 6.788   | Benzene                                 | 1.7     | 22  | 27     |
| 8.790   | 4-Penten-2-one, 4-methyl-               | 1.7     | -   | -      |
| 10.361  | 3-Penten-2-one, 4-methyl-               | 5.9     | 41  | 6.2    |
| 12.013  | 2-Pentanone, 4-hydroxy-4-methyl-        | 41.0    | 40  | 49     |
| 12.982  | Ethylbenzene                            | -       | -   | 26     |
| 14.296  | Styrene                                 | -       | -   | 29     |
| 14.943  | 2-Cyclopenten-1-one, 2-methyl-          | -       | -   | -      |
| 15.861  | Benzene, (1-methyl)ethyl-               | -       | -   | 37     |
| 18.500  | Phenol                                  | 2.3     | -   | -      |
| 20.922  | 2-Cyclopenten-1-one, 2-hydroxy-3-methyl-| -       | -   | -      |
| 21.578  | 2-Cyclopenten-1-one, 2,3-dimethyl-      | -       | -   | -      |
| 22.240  | Phenol, 2-methyl-                       | 2.4     | 29  | -      |
| 23.242  | Phenol, 3-methyl-                       | -       | -   | 25     |
| 23.858  | Phenol, 4-methyl-                       | 37      | 36  | -      |
| 24.217  | Phenol, 2-methoxy-                      | 77      | 78  | 82     |
| 26.990  | Phenol, 2.5-dimethyl-                   | 39      | -   | -      |
| 27.965  | Phenol, 2.3-dimethyl-                   | -       | -   | 11     |
| 28.641  | Phenol, 2-methoxy-3-methyl-             | -       | -   | -      |
| 29.392  | Phenol, 2-methoxy-4-methyl-             | -       | 107 | 136    |
| 29.999  | 2-Methoxy-5-methylphenol                | 10.3    | -   | -      |
| 33.507  | Phenol, 4-ethyl-2-methoxy-              | 9.5     | 92  | 106    |
| 33.807  | 1,2-Benzenediol, 4-methyl-              | -       | 27  | -      |
| 36.632  | Phenol, 2-(1,1-dimethylethyl)-4-methyl- | -       | -   | 2.8    |
| 37.029  | 3-Allyl-6-methoxyphenol                 | -       | -   | -      |
| 37.044  | Eugenol                                 | -       | -   | -      |
| 37.530  | Phenol, 2-methoxy-4-propyl-             | 7.3     | 8.5 | 11.4   |
| 39.628  | 1,4-Methanoazulene, decahydro-4,8,8-     | -       | -   | 1.8    |
| 41.123  | Phenol, 2-methoxy-4-(1-propenyl)-,(E)- | 2.5     | 28  | -      |
| 42.704  | Ethanone, 1-(3-hydroxy-4-methoxyphenyl)-| -       | -   | -      |
| 44.499  | Propan-2-one, 1-(4-isopropoxy-3-        | -       | -   | -      |
| 44.506  | 2-Propanone, 1-(4-isopropoxy-3-methyl-  | -       | -   | -      |
| 49.365  | Benzene, 1,1'-(1,3-propanediyl)bis-     | -       | -   | 6.5    |
| 61.089  | 1-Phenanthrene-carboxaldehyde           | 37      | 46  | 4.0    |
| 62.329  | 4b,8-Dimethyl-2-isopropylphenanthrene,  | 43      | 53  | 5.8    |
| 63.369  | Phenanthrene, 2,5-dimethyl-             | 2.4     | 32  | -      |
| 64.796  | 10,18-Benzobicyclo[5.7.0]10,11,13-       | 33.9    | 39  | 3.8    |
| 66.615  | 9-Ethyl-10-methylanthracene             | 26      | 26  | -      |
| 68.518  | Phenanthrene, 1-methyl-7-(1-methyl-     | 10.2    | 127 | 10.9   |
| 71.233  | 8-Isopropyl-1,1-dimethylphenantherne     | 24      | 25  | -      |
| 71.805  | 1-Phenanthrene-carboxylic acid          | 52      | 47  | 6.0    |

Area (%)
The relationship of atomic ratios by Van Krevelen diagram of liquefied products via thermal co-treatment of 25% plastic mixture in substrate: 300 °C for 30 min with different plastics and solvents.

Results indicated that thermal co-treatment of the PS mixture with all solvents decreased the O/C and H/C atomic ratios from 0.20 to 0.06 and 1.15 to 1.35, respectively. Further, thermal co-treatment with PE and PP also decreased the H/C and O/C atomic ratios as compared to the substrate. As indicated in Fig. 12, the HHVs of liquefied products generated from the 25% PS mixture were 39.1 (acetone), 36.4 (THF) and 40.1 (hexane). Moreover, ketone fractionation was observed in the liquefied product during thermal co-treatment with acetone (Fig. 10). Therefore, interaction with acetone reduced the carbon content of the liquefied product. Furthermore, the HHVs of liquefied products generated from thermal co-treatment with acetone and hexane were not significantly different. However, the liquid yields from acetone and hexane indicated a significant difference of 10.0%. Energy recovery of liquefied products has shown in Table 5. The results showed that the highest energy recovery is the liquefied product of 25% PS mixture with THF. However, the properties of the liquefied product...
acetone was enough fluent. THF solvent had affected to all solvents in contrast to PE and PP. Furthermore, addition degraded components and acetone resulted in ketone CO2 containing gaseous product. The interaction between case of acetone. Consequently, thermal co-treatment of such as ethylbenzene, (1-methylethyl)benzene and 3-penten-2-one. In addition, the synergetic effects of co-treatment with THF at 300 °C for 30 min because high viscous and coagulating liquefied product by THF were unsuitable for use as liquid fuel feedstock was obtained after solvent removal. Liquefied product with acetone was enough fluent. THF solvent had affected to prevent the formation of solid residue to keep relatively large oligomers from PS degradation as compared to the case of acetone. Consequently, thermal co-treatment of the 25% PS mixture with acetone provided optimal conditions for homogenization conditions and should be further studied.

4. Conclusions

Thermal co-treatment of heavy tar and plastics with solvent at 300 °C can improve the characteristics of feedstock for subsequent liquid fuel production. The results indicated that deoxygenation of the substrate produced CO2 containing gaseous product. The interaction between degraded components and acetone resulted in ketone fractionation to generate compounds such as 4-methyl-3-penten-2-one. In addition, the synergetic effects of co-feeding increased the concentrations of hydrocarbons such as ethylbenzene, (1-methylethyl)benzene and 1,1’-(1,3-propanediyl)bis-benzene. The highest quantity of liquefied product (97.4%) was obtained by thermal co-treatment with THF at 300 °C for 30 min. Co-feeding of heavy tar and PS indicated the highest homogenization for all solvents in contrast to PE and PP. Furthermore, addition of solvents prevented the formation of solid residues, which were the lowest for THF (~2.6%). Fractionation of the liquefied products indicated that phenol and its derivatives were the primary components. The results of this study suggested that thermal co-treatment of the 25% PS mixture with acetone provided optimal conditions for homogenization of the liquefied product.

Table 5  Energy recovery of liquefied production by thermal co-treatment of 25% plastic mixture with different conditions (plastic types and solvents) at 300 °C for 30 min

| Substrate | Solvent | Energy recovery |
|-----------|---------|-----------------|
| 25% PE    | Acetone | 0.42            |
|           | THF     | 0.47            |
|           | Hexane  | 0.31            |
| 25% PP    | Acetone | 0.46            |
|           | THF     | 0.60            |
|           | Hexane  | 0.34            |
| 25% PS    | Acetone | 0.97            |
|           | THF     | 1.01            |
|           | Hexane  | 0.85            |

4. Conclusions

Thermal co-treatment of heavy tar and plastics with solvent at 300 °C can improve the characteristics of feedstock for subsequent liquid fuel production. The results indicated that deoxygenation of the substrate produced CO2 containing gaseous product. The interaction between degraded components and acetone resulted in ketone fractionation to generate compounds such as 4-methyl-3-penten-2-one. In addition, the synergetic effects of co-feeding increased the concentrations of hydrocarbons such as ethylbenzene, (1-methylethyl)benzene and 1,1’-(1,3-propanediyl)bis-benzene. The highest quantity of liquefied product (97.4%) was obtained by thermal co-treatment with THF at 300 °C for 30 min. Co-feeding of heavy tar and PS indicated the highest homogenization for all solvents in contrast to PE and PP. Furthermore, addition of solvents prevented the formation of solid residues, which were the lowest for THF (~2.6%). Fractionation of the liquefied products indicated that phenol and its derivatives were the primary components. The results of this study suggested that thermal co-treatment of the 25% PS mixture with acetone provided optimal conditions for homogenization of the liquefied product.

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