

УДК 541.64;678.577

The Scope for Distillable Liquids Generation from Biomass and Plastics Waste Via Pyrolysis

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Received 15.01.2008, received in revised form 15.03.2008, accepted 10.04.2008

Thermal behavior of wood biomass, synthetic polymers and their mixtures has been studied in a rotating autoclave in a temperature range 360 - 450°C. The effects of reaction conditions, biomass and polymers origins on the degree of mixtures conversion as well as on the products yield and composition were established and discussed. In the co - liquefaction processes the interaction between fragments of wood and polymers thermal decomposition took place. This resulted in a non additive increase of the wood/ polymers conversion degree and of the yield of distillate fractions.

Chemical composition of the distillate liquid products (b.p. < 180°C) obtained by co-pyrolysis of polyolefins / wood biomass mixtures under inert and hydrogen atmospheres was established by GC-MS. Heavy liquids (b.p. > 180°C) were investigated by FTIR, ¹H NMR, GC-MS. The preliminary separation of heavy liquids into different fractions by open LC and TLC methods had been used. Some futures of polymer and biomass thermal conversion during co-pyrolysis process were discussed.

Keywords: wood biomass, synthetic polymers, pyrolysis, distillate liquid products.

Introduction

Upgrading of wood biomass residues as well as polymers waste is an important problem of environmental protection. Much attention has been recently paid to pyrolysis techniques as method for fuel or liquid chemical compounds generation from such types of materials [1-7]. It is known that the polyolefinic polymers can be readily thermally decomposed to gaseous and liquids hydrocarbons. Pyrolysis of the polymers in

an inert atmosphere or under vacuum at elevated temperatures gives heavy paraffins and olefins as a major reaction product. Mainly gaseous and light hydrocarbons are obtained during polymer thermolysis at higher temperatures (above 700°C). Free radical degradation mechanism of the polymers chain is proposed to explain the patterns of pyrolyzates [8-9]. In this mechanism it is assumed that the degradation of polymers is a chain reaction involving the thermal initiation,

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propagation, intermolecular and intermolecular transfer and termination of radicals.

Wood biomass pyrolysis produces three types of products: gases, tar or heavy oil fraction containing volatile species, and char fractions. Pyrolysis tar contains a very wide range of complex organic chemicals: organic acids, alcohols, aldehydes and ketones, phenols, ethers, and in a smaller degree saturated and unsaturated hydrocarbons [10,11]. The investigation of pyrolysis of cellulose, the major component of wood, has shown that liquids are produced through free radical generation by the thermal cleavage of oxygen containing chemical bonds [11,12]. During this unzipping reaction of the cellulose chain, dehydration of carbohydrate units can occur, which leads to the formation of char. In the pyrolysis process under hydrogen atmosphere a higher yield of liquid products is obtained because the char formation is suppressed and recondensation or recombination of thermal cracking products is reduced.

Polyolefinic polymers, like polyethylene and polypropylene, contain approximately fourteen weight percent of hydrogen. These materials could provide hydrogen during thermal co-processing with wood biomass and can lead to an increase of liquid production. There are some data indicating that the mixture of wood with polyethylene and polypropylene can be successfully converted into liquids using pyrolysis and hydrolysis techniques [13,14]. The yield of these products depends on process operating conditions. Some results also indicated synergistic effects for co-liquefaction of coal - plastic mixtures in the form of enhanced oil yields [15 -17].

The present paper summarises experimental investigations of wood biomass, synthetic polymers and their mixtures pyrolysis in autoclave condition. The influences of wood biomass and plastic origins, catalysts additives and process

parameters on the conversional degree, products yield and composition are discussed.

Experimental

The feedstock materials used in this work included beech wood, pine wood, cellulose (Avicel from Merck CAS N° 9004-34-6) and hydrolytic lignin (Krasnoyarsk Hydrolytic Company, Russia) as well as commercially available (Tomsk Petrochemical Company, Russia) medium density polyethylene (PE) with average molecular weight number (M_n)=20000, atactic-polypropylene (aPP) with $M_n = 900$, isotactic-polypropylene (iPP) with $M_n = 10000$. In hydrolysis experiments, haematite and pyrrhotite ore materials were used as a catalyst. In order to increase the catalyst activity their mixture with water (25 wt. %) were treated in a tensile energy planetary activator mill AGO-2 during 30 seconds at centrifugal acceleration of grinding bodies (balls) - 600 m·s⁻². Such treatment results in the increase of catalyst dispersion and changes their structure [18 – 19].

Liquefaction reaction of plastics and wood biomass alone and co-processing reaction of biomass and plastics were performed using 250 cm³ stainless steel rotating autoclave. The feedstock materials and catalyst were loaded into autoclave, pressurized with argon (pyrolysis) up to 0.1 MPa or with hydrogen (hydrolysis) up to 3.0 MPa and then heated. The duration of thermal treatment was 1-3 h. in the temperature range of 360-480°C. Generally the working pressure in autoclave, at 400°C, was approximately 3.0 MPa and 6.0 MPa for pyrolysis and hydrolysis experiments, correspondingly.

Light liquid products (with equivalent boiling point at atmospheric pressure below 180°C) were distilled from the autoclave in vacuum at ambient temperature and frozen by liquid nitrogen. These products were separated in light liquid (fraction 1) and water fractions by decantation. The heavier products were extracted with benzene, and

separated (after solvent removal) by vacuum distillation into fractions of equivalent boiling point at atmospheric pressure of 180 - 350°C (fraction 2) and distillation residue (fraction 3). The degree of feedstock conversion was calculated from the difference between the weights of initial mixture and solid residue, insoluble in benzene.

The distillable liquids were analysed using an Agilent 6890 series GC system supplied with 5973 mass selective detector. Fractions 1 were separated on a Optima I capillary column (50m – 0.2 mm i.d. – 0.5 µm film thickness OV-1), fractions 2 on a HP – 5MC capillary column (30m – 0.25 mm i.d. – 0.25 µm crosslinked 5% PHME Siloxane). The mass spectrometer operated at 70eV in EI mode.

Heavy liquid fractions were fractionated by a classical open column liquid chromatography method [20]. The glass column (i.d. 1.5 cm) was filled with n-hexane (1/3 in volume) and the Silicagel (60-230 Mesh, MERK) was putted in. Preliminary, silicagel (8.5 g) was dried at 110°C during 8 hours and then distilled water (10 to 15 % in weight) was added to the Silicagel. The sample (≈ 0.34 g) was dissolved in (0.5 to 1 ml) dichloromethane and placed onto the top of the column. The elution consequence was: hexane, dichloromethane, dichloromethane/tetrahydrofurane mixture (90/10 in weight) and methanol. Then, solvent from the different fractions collected were evaporated by rotary

evaporator and the residue was placed into a desiccator till constant weight.

Results and discussion

Table 1 presents the data of the beech/aPP mixture conversion degree and the yield of the reactions products, obtained during the mixture pyrolysis at the different temperature in inert (Ar) atmosphere. It can be seen that the conversion degree increases slightly with growth of the temperature in the studied range (360-450°C). The main effect of temperature increase is higher amounts of gas and light liquid, whilst the yields of water and heavy liquid fractions continuously decrease. The maximum yield of light liquid (18.5 wt.%) is obtained at 400°C. These results could be explained by the cracking of light liquids from aPP and wood to gas at temperature above 400°C. Obtained results are typical for all mixtures of studied biomass and polymers.

In order to study the influence of the biomass origin on the degree of biomass / plastic mixture conversion and product yields, some experiments were carried out at 400°C with fixed composition (biomass/plastic 50:50 in weight). Among the studied biomass samples, the lignin and aPP mixture allows as expected the lowest yields of water and light liquid hydrocarbons fraction (Table 2).

In the case of cellulose/aPP the two times increase of water and light fraction yields are observed in comparison with lignin/aPP. The

Table 1. Influence of pyrolysis temperature on the beech wood / a-PP mixture (50:50 in weight) conversion degree and the yield of products

| Temperature, °C | Conversion degree, wt. % | Yield of products, wt. % | | | |
|-----------------|--------------------------|--------------------------|-------------------------|--------------------------------------|-------|
| | | Water fraction | Hydrocarbons fraction 1 | Hydrocarbons fraction 2 + fraction 3 | Gases |
| 360 | 72 | 20.4 | 4.5 | 39.1 | 8.3 |
| 380 | 75 | 19.6 | 12 | 33.1 | 10.3 |
| 400 | 79 | 18.7 | 18.5 | 31.6 | 9.8 |
| 430 | 80 | 16.1 | 16.6 | 29.6 | 17.7 |
| 450 | 79 | 15.8 | 14.8 | 26.8 | 21.6 |

Table 2. Influence of biomass origin on the biomass/aPP (50:50 in weight) conversion degree and yield of pyrolysis products (argon atmosphere at 400°C)

| Biomass origin | Conversion degree, wt. % | Yield of products, wt. % | | | |
|-------------------|--------------------------|--------------------------|-------------------------|--------------------------------------|-------|
| | | Water fraction | Hydrocarbons fraction 1 | Hydrocarbons fraction 2 + fraction 3 | Gases |
| Beech wood | 82.7 | 18.5 | 18.7 | 31.6 | 9.8 |
| Pine wood | 76.4 | 17.1 | 23.4 | 24.4 | 11.5 |
| Hydrolytic lignin | 67.6 | 12.5 | 17.1 | 27.7 | 10.3 |
| Cellulose | 82.7 | 24.0 | 25.0 | 25.6 | 8.1 |

mixtures of beech and pine wood with aPP give similar yields of char and gaseous products. But the yield of light hydrocarbon fraction of pine/aPP products is higher and, accordingly, the yield of heavy fraction is lower than beech/aPP run. These data indicate that the difference between the co-pyrolysis of pine and beech with plastic is not simply connected with elemental composition, content of wood components or thermal decomposition profiles but probably, can be explained by specific chemical properties of these two kinds of wood (hardwood and softwood).

Fig. 1 illustrates the influence of feedstock composition on the co-processing products yield. It can be seen, that the yield of liquid hydrocarbon fractions increases with the plastic concentration.

But, the distribution between light and heavy liquids strongly depends on the biomass/polymer ratio. The maximum yield of light hydrocarbons liquids is obtained for the 20 - 30 wt.% biomass/70 - 80 wt.% polymer mixtures (37.1 wt.% for cellulose/aPP pyrolysis, 45.3 wt.% for pine wood/PE catalytic hydro-pyrolysis). Clearly, the yield of light liquids (in both cases) are more than 2 times higher, as compared to the expected ones (dotted line, Fig. 4), calculated as a sum of light liquid fractions produced by pyrolysis of each separated component.

The gaseous products of the pyrolysis of aPP alone contain more than 75% mol. of olefins. In the gaseous products of the beech/aPP mixture (20/80 weight ratio) only approximately 8 wt.%

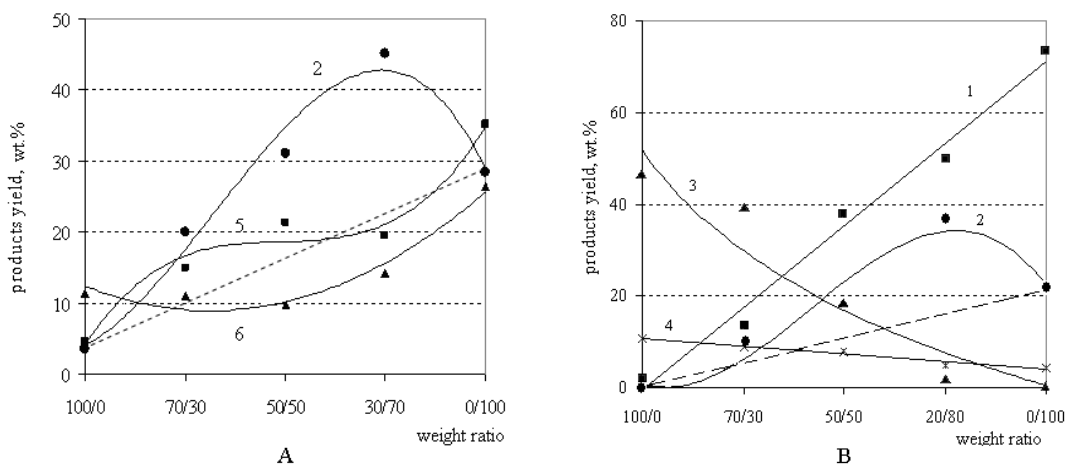


Fig.1. Changes of the yield of co-processing products: (1) - the sum of fraction 2 and fraction 3, (2) – hydrocarbon fraction 1, (3) – water fraction, (4) – gases, (5) – hydrocarbon fraction 2, (6)- fraction 3 vs. feedstock composition; (A) - pyrolysis of pine wood/PE mixture under a hydrogen pressure in a presence of haematite catalyst (5wt.%), (B) – pyrolysis of cellulose / aPP mixture under an argon pressure. Temperature - 400°C

of the unsaturated hydrocarbons were detected. Taking these data into account, it is possible to suppose that the olefinic products from aPP thermal conversion react with some products from cellulose and beech depolymerization. The result is the light hydrocarbon liquids formation. This assumption shall explain the synergistic effect observed in the pyrolysis of the biomass/aPP mixtures. According to [9], the solid products from wood decomposition certainly also play a role on some depolymerisation pathways of the polypropylene leading to light hydrocarbons liquids.

The GC-MS data of the light distillable fractions 1 (b.p. < 180°C) produced from mixtures of pine wood with PE and iPP during their hydrolysis are reported in Fig. 2.

For comparison, the data obtained in the mixture pyrolysis under inert atmosphere are given. The abundances of the products are listed as area percentages of the total ion intensity. High olefins contents (near 40 wt.%) are observed for co-pyrolysis in an inert atmosphere. If hydrogen atmosphere slightly reduces these values for both polymers, addition of the catalysts leads to their drastic reduction. A remarkable point is the increase

of aromatic compounds in hydrogen atmosphere. Fig. 3,4 illustrates the typical distribution of the individual hydrocarbons in the light fractions (iPP and PE). In both cases, the maximum abundance is observed for C9 hydrocarbons. For iPP, C6 and C12 secondary maximum are also noted. On the contrary, for PE a more smooth distribution is observed. These results are connected to the structure of the starting polymers and can be explained by classical radical mechanisms of degradation [9,21].

Fractions 2 can not be investigated directly by GC/MS. Consequently, these fractions were characterised according to the open column chromatography adapted from [22]. Briefly, fractions 2 obtained from the biomass/polymers mixture pyrolysis under an argon and a hydrogen pressure mainly content hexane (70 – 80 wt.%) and THF (9 – 18 wt.%) eluted products. Analysed by ¹H NMR, the hexane eluted fraction are characterised by low amount the both: aromatic protons and olefinic protons (< 5 % of the total protons) and a large majority of aliphatic protons.

The chemical composition of these fractions is relatively simple: mainly paraffins and olefins as identified by infrared spectroscopy and GC-

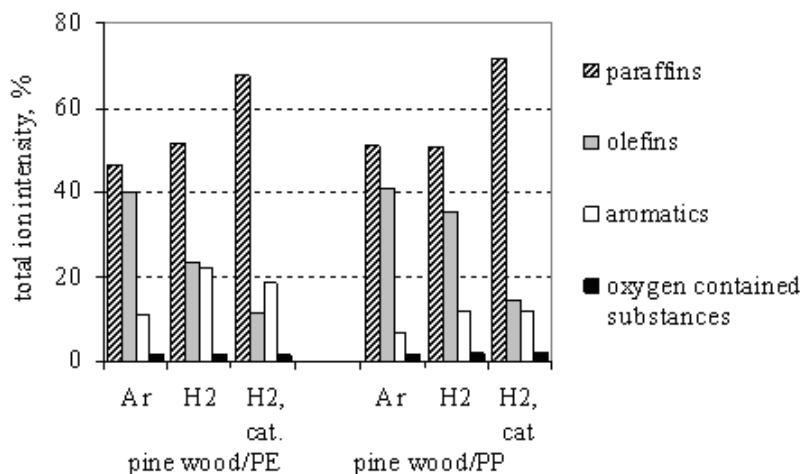


Fig. 2. Changes of the fraction 1 (b.p. < 180°C) composition vs. co-pyrolysis of pine wood/polymer mixtures (50/50 in wt) experimental conditions: Ar – argon atmosphere, H₂ – hydrogen atmosphere, cat - haematite catalyst (5 wt.%). Temperature - 400°C

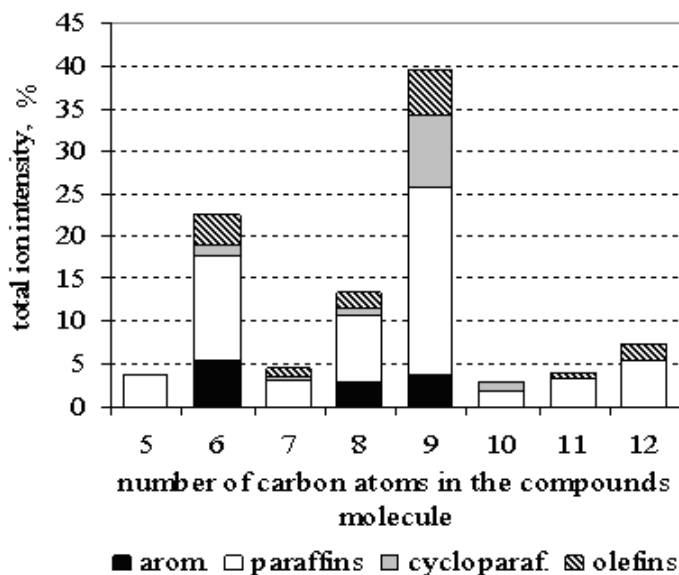


Fig. 3. GC-MS data of the hydrocarbons distribution in the fraction 1 (b.p. < 180°C) of pine wood/ iPP mixtures (50/50 in wt) co- hydrolysis at 400°C in a presence of haematite catalyst (5 wt.%)

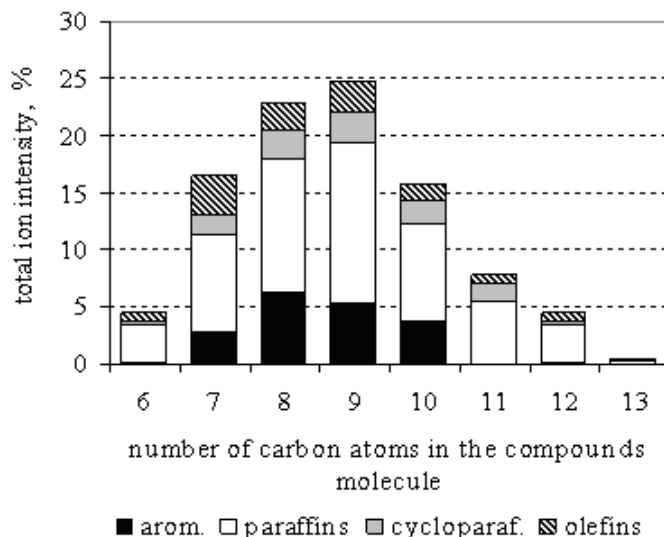


Fig. 4. GC-MS data of the hydrocarbons distribution in the fraction 1 (b.p. < 180°C) of pine wood/ PE mixtures (50/50 in wt) co- hydrolysis at 400°C in a presence of haematite catalyst (5 wt.%)

MS. According to GC-MS data, these products of PE/pine wood mixture pyrolysis consist mainly of normal paraffins in $C_{11} - C_{31}$ range. In catalytic or in not catalytic conditions of iPP/ wood mixtures hydrolysis large amounts of structural isomers were found and, consequently, the obtained chromatograms were complex. Indicatively, the identified peaks represent only

80 % of the total peaks areas. The results for both conditions (and polymers) are reported in Fig. 5.

Some very interesting trends can be observed. First of all, the decreases of the olefins and cycloparaffins contents under catalytic action. The influence of the catalyst on the hydrogenation of olefins is clearly evidenced. It is also essential to note that the catalyst disfavors the mechanisms

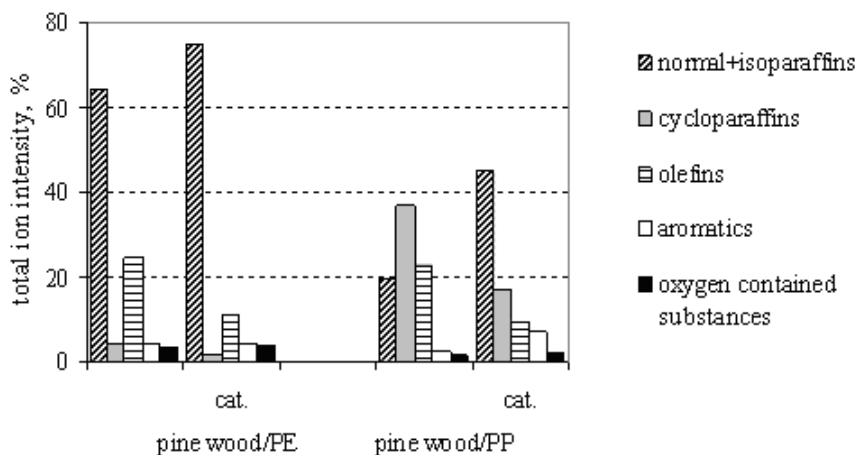


Fig.5. Influence of the haematite catalyst additives (5 wt.%) on the hexane eluted products of fraction 2 (b.p. 180 – 350°C) composition. Hydropyrolysis of pine wood/polymers mixtures (50/50 in wt.) at 400°C

leading to cycloparaffins production. The aromatic contents is slightly changed for all the studied fractions where alkyl substituted phenyl, phenol, are found.

The infra red spectra of the DCM products of fraction 2 present some bands corresponding to O-H vibration (3600- 3200 cm^{-1}), carbonyl groups (1650 – 1750 cm^{-1}) and C-O vibration (1350 – 1000 cm^{-1}). It seems reasonable to consider that these fractions are, at least in part, composed of liquids from biomass.

Conclusion

As the present study has demonstrated, the mixtures of the different types of biomass wood and polyolefinic polymers can be radically converted to distillable hydrocarbon fractions by pyrolysis under inert or hydrogen atmospheres. At 400°C the maximum yield of liquid products has been observed. The origin of biomass as well as the type of polymers play an important role on the final products distribution. Iron ore material modified by a mechanochemical treatment demonstrates a

catalytic activity in the hydropyrolysis of wood/polyolefinic polymers mixtures. A significant increase of the distillable products yield (by 14-21 wt %) is observed when using these catalysts.

During co-processing of biomass with polymer some synergistic effects are established. For pyrolysis of the mixtures with polymer content higher than 50 wt.%, non additive phenomena occur leading to higher light liquids formation. Biomass promotes β -olefins production from the polymers. In the co – hydropyrolysis process the non additive increase of the wood/polymer mixtures conversion degree and of the distillable fractions yields takes place.

To resume, the co-pyrolysis processes have a good potential for the environmentally friendly transformation of lignocellulosic and plastic waste to distillate hydrocarbon fractions. The chemical composition of these products seems to be quite suitable for use as a valuable raw material for engine fuels and chemicals production.

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