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THERMAL CRACKING OF MIXTURES OF PLASTICS AND WOODY MATERIAL

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Abstract

This work aimed to study the recovery of two types of waste by the process of thermal cracking (copyrolysis). The obtained results show that the adding of plastic mix improves the overall efficiency of the slow pyrolysis of woody material. Therefore, it was possible to achieve higher gaseous yields and less solid product than in the carbonization of woody material. The gas products had energetic contents superior to that of producer gas, and the obtained solid fractions showed heating values higher than some coals. The obtained liquids showed heating values similar to that of heating fuel oil. The effects temperature and reaction time in the product yields and composition were also studied.

Keywords: Thermal cracking; pyrolysis; plastics; biomass; waste.

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1. Introduction

Plastics and biomass wastes are two kinds of residues that presently pose difficulties when addressing their final post use destination. The alternatives employed today are incineration and landfill deposition. However, these are far from optimal treatment options, because they can raise environmental issues, like toxic and greenhouse gas emissions, leachates, etc., besides wasting their organic content that could be otherwise valuable in several applications. One of the promising ways of taking profit of the energetic and organic value of wastes is pyrolysis.

Pyrolysis is the thermal degradation of organic waste in the absence of oxygen to produce a carbonaceous char, oil and combustible gases. How much of each produced is depend on the process conditions, particularly temperature and heating rate. Waste materials are composed of complex chemical compounds, for example, municipal solid waste contains paper and cardboard which are composed of large, complex polymeric, organic molecule chains such as cellulose, hemicellulose and lignin. Similarly, wastes such forestry wastes and biomass are also mainly composed of cellulose, hemicellulose and lignin polymeric molecules. Plastics are also composed of large polymers chain. The process of thermal degradation or pyrolysis of such materials in the absence of oxygen, results in the long polymer chains cracking to produce shorter molecular weight chains and molecules. These shorter molecules result in the formation of the oils and gases characteristic of pyrolysis of waste. The exact mechanisms of thermal cracking of waste are not clear.

The process conditions are altered to produce the desired char, gas or oil end product, with the cracking temperature and heating rate having the most influence on the product distribution. Pyrolysis systems for municipal solid waste, plastics, tyres, composite plastics, sewage sludge, textile waste and biomass have been investigated [1-3].

Several authors have studied plastics pyrolysis and have demonstrated the potentialities of this technology to process plastic wastes [1,4-8]. The steam cracking (copyrolysis) of naphtha with oils/waxes from thermal decomposition of a individual and mixture polymers in different blends, studied by us [5-7], showed that the yields of the desired alkenes (ethene, propene), according to polymer type, increased or only slightly decreased compared to the yields from naphtha. Utilization of oils/waxes obtained from thermal cracking of individual or cracking of mixed polymers for the production of automotive gasoline and diesel fuels was overviewed [8].

Fast pyrolysis has been proven to be adequate process to produce a liquid product from woody materials, with suitable fuel properties (“biooil”) in contrast to the typical slow pyrolysis method of carbonization to produce char [9-13]. However, some properties of this bio-oil restrict its direct use in a diesel engine, so research is still undergoing to improve these properties (bio-oil upgrading) [14-15].

In a previous work [16] pyrolysis of woody material was studied the effect of experimental conditions on products yield and composition.

In the present work two types of waste : plastics and biomass were pyrolyzed the aim of studying the experimental conditions that maximized liquid yields. The aim of mixing plastic with biomass wastes was to improve the liquid fraction of the products, and to evaluate the H-donor effect of the plastic, as by pyrolysis a liquid medium will be produced which may facilitate mass and heat transfer and consequently farther pyrolysis reactions. On the other hand, the presence of plastics might also improve liquids properties and its behaviour as a fuel. A mixture of PE, PP, PS, PET and PVC, the major plastic components of the Municipal Solid Wastes (MSW) was used in the present study. Beech wood was the biomass species selected for this work, because it is the most abundant variety in Slovak forest. Mixtures with these two wastes in different compositions were pyrolyzed to identify and to take profit of any synergistic effects.

2. Experimental

2.1 Raw materials

The feedstocks used in our work were obtained from the Slovak Republic. The characteristic for all feedstocks have been evaluated for the temperature 25°C [16,18].

2.1.1. Polymers

Main characteristic of used polymers is in table 1. Polymers were virgin plastics in the form of pellets, except of PET (bottle) and PVC (powder).

Table 1 Characteristic of used polymers

Polymer	$\bar{M}_w$	$\bar{M}_n$	ρ, kg.m^{-3}	Producer
HDPE	33 800	6 950	950	Slovnaft, a.s.
LDPE	292 000	22 000	919	Slovnaft, a.s.
LLDPE	112 110	30 300	919	Slovnaft, a.s.
PP	200 000	65 000	903	Slovnaft, a.s.
PS	-	135 135	1 050	Plastika, a.s.
PVC	173 000	86 500	1 380	Plastika, a.s.
PET	62 500	25 000	920	waste

Polymers are virgin plastics in the from of pellets, except of PET (bottle) and PVC (powder). The composition of seven components polymer blend used in feedstocks is shown in Table 2.

Table 2. The composition of polymer blend

Plastic sample	Weight [g]	%wt.
HDPE	2.9	34.6
LDPE	1.5	17.3
LLDPE	1.5	17.3
PP	0.8	9.6
PS	0.8	9.6
PET	0.9	10.6
PVC	0.1	1.1
Total	8.5	100.0

2.1.2 Biomass

Beech wood sawdust were used as biomass. Some characteristics of the used wood biomass are given in Table 3. The particle size of the wood biomass was from 0.1 to 0.5 mm (sawdust). The beech wood used our work was obtained from the Slovak Republic. The ash content of beech wood amounts only 0.34 %wt. [16, 18].

Table 3. Some characteristics of the beech wood

Elemental composition (%wt.)[a]		Wood components distribution (%wt.)[a]	
C	45.9	Cellulose[b]	46.4
H	6.0	Lignin	25.3
N	0.2	Hemi cellulose	22.4
S	0.2	Water soluble	5.1
O	47.7	Ether soluble	0.8

a Dry ash-free basis, b By differences

2.2 Thermal cracking of blends

We used a similar apparatus as in our previous work [5], without cooler operating at 90°C. We fed the batch reactor with 8.5 g polymer mix and 8.5 g sawdust of the beech wood and closed it. The experiments were run in inert atmosphere. The flow of nitrogen (inert) gas was 50 ml.min^{-1}. Thermal cracking took 103 min. at 450°C and 116 min. at 500°C. The following program for thermal cracking of polymer and wood blend was used: heating rate 16.5°C.min^{-1} to 350°C, 8 min. temperature stabilization, heating rate of 9°C.min^{-1} up to 440°C, heating rate of 7.5°C.min^{-1}up to 480°C. However final real temperature in the reactor was 450°C. The temperature was controlled by thermocouples. The convenient rate heating and duration of polymer and biomass blends cracking for the production high yields of liquid products was determined to be 103 min. and 116 min. as result of the optimization procedure. Detailed description of thermal cracking is given in literature [5, 8]. Obtained products were : gas collected in the gas sample, oil and water layers of liquids in the separator and brown residue in the reactor. In many countries, plastic is collected from commercial and industrial sources as separate plastic fractions, much of which is recycled directly back into plastic product manufacturing process. Although plastic make up between 5 and 15 %wt. of municipal solid waste (MSW) it comprises 20-30% of the volume [2]. There are five main plastics which arise in Slovakia municipal solid waste. PE (6 %wt.), PP (9%), PS (9%), PET (10%), PVC 1%)rest (PA, ABS, PMMA, and others) (6%) [17].

2.3. Analysis of gaseous and liquid products from thermal cracking

Analysis of the gases obtained from thermal cracking of polymer blend and beech wood performed with the gas chromatograph Hewlett Packard HP 6890+. The three-PLOT chromatographic column system consists of two parallely installed detectors FID and TCD and of three switching valves. Helium was used as a carrier gas. The temperature in the injection chamber was 150°C. The time of analysis was about 40 min.

The liquids obtained from thermal cracking were analyzed with the gas chromatograph CHROM 5. The gas chromatograph system consist of the DB-PETRO column and the FID detector. Helium was used as a carrier gas. The temperature in the injection chamber was 240°C. The time analysis was about 80 min. The analytical procedure was described in detail in [5, 6].

2.4. Results and discussion

The thermal cracking of mixtures of plastics (8.5 g) and woody material (8.5 g) was performed under atmospheric pressure at 450°C and 500°C. The products of thermal cracking were classified into three groups : gas, liquid (oil and water) and solid residue. Table 4 shows the yields of thermal cracking products. Thermal cracking of mixtures of plastics and forestry biomass resulted in 30.3 – 40.7 %wt. of gas, 40.4 – 43.8 %wt. of liquid and 18.9 – 25.9 %wt. of solid residues.

It can be observed in Table 4 that an increase in reaction temperature seems to decrease liquid and solid yield and to favor the real case of gaseous compounds, probably because the rise of reaction temperature favored cracking reactions, converting longer and heavier molecules, liquid at standard conditions of temperature and pressure into smaller molecules. The results in Table 3 led to selection of 450°C for the next experiments sets, as the objective is to maximize liquids production.

Table 4 Products yield of thermal cracking of mixtures of plastics and woody material

Temperature, °C	450			500		
	Y (mass)			Y (mass)		
	Liquid	Gas	Solid residue	Liquid	Gas	Solid residue
g	7.5	5.1	4.4	6.9	6.9	3.2
%wt.	43.8	30.3	25.9	40.4	40.7	18.9

The samples of the released gases were taken at end temperature 450°C, and repeatedly at 350, 400 and 450°C, and also one hour after reaching the temperature 450°C (Table 5). In the case of the end temperature 400, 450 and 500°C, but also one hour after reaching the temperature 500°C (Table 6). It can be seen from the gas chromatography analysis that the pyrogas in its considerable portion is composed of carbon oxide, the generation of which decreases with increasing temperature and reaction time. In case of temperature 450°C the fall was seen from 91.3 %wt. to 72.9 %wt. and at 500°C the fall went from

90.3 to 18.4 %wt.. At 450°C the amount of carbon dioxide culminated within 43 minutes (9.5 %wt.), at 500°C it unambiguously decreased (from 3.0 to 0.2 %wt.). During the reaction conditions discussed no discharge of hydrogen was noticed. On increased temperature from 450 to 500° C, there occurs a decrease both in the amount of carbon monoxide and carbon dioxide . However, as to amount, at both temperatures carbon monoxide dominates. It is surprising that in the case of pyrolysis of only wood, the situation is actually the opposite [16]. In the case of pyrolysis of mixture of polymer wastes and wood biomass at 450°C, the ratio $CO_2/CO = 0.07$, but at thermal cracking of woody material the ration $CO_2/CO = 1.5$.

Table 5 Product distribution (%wt.) of components in gases obtained by thermal cracking of plastics and woody material at 450°C

Temperature, °C	350	400	450	450	Average composition of gas
Time of experiment, min	22	31	43	103	
Components, %wt.	Composition, %wt.				
Carbon dioxide	1.5	7.6	9.5	4.2	5.7
Carbon monoxide	91.3	84.4	76.6	72.9	81.3
Methane	0.3	1.8	5.2	8.7	4.0
Ethane	0.3	0.3	1.4	3.0	1.2
Ethylene	0.4	1.1	2.4	4.3	2.0
Propane	0.4	0.2	0.6	1.2	0.6
Propene	1.0	0.4	1.4	3.0	1.5
Methylpropane	tr.	tr.	tr.	tr.	tr.
Butane	0.3	tr.	0.1	0.3	0.2
trans-2-Butene	0.1	tr.	tr.	0.1	0.1
1-Butene	0.5	0.1	0.2	0.4	0.3
Methylpropene	0.2	0.1	0.3	0.4	0.3
cis-2-Butene	0.1	tr.	tr.	tr.	tr.
C_4-hydrocarbons	2.2	3.1	1.4	0.8	1.9
Pentane	0.7	0.9	0.7	0.6	0.7
1,3-Butadiene	0.1	tr.	0.1	0.1	0.1
2-Methyl-2-butene	0.1	tr.	tr.	tr.	tr.
1-Pentene	tr.	tr.	tr.	tr.	tr.
C_5-hydrocarbons	0.1	tr.	0.1	0.1	0.1
Benzene	0.3	tr.	tr.	tr.	0.1

tr. - traces

The rising temperature definitely increased the discharge of gaseous low-molecular alkanes and alkenes. In the gaseous products from both experiments on growing temperature, the amounts of low-molecular alkanes increased. The amount of higher than C3-hydrocarbons remains rather minute. Comparisons of the average composition of gases at 450 and 500°C show that on pyrolysis at higher temperature not only less carbon oxides is evolved but also a greater amount of low-molecular pyrolytic products gets evolved. Even comparisons of evolutions of gaseous pyrolytic products from decomposition of only mixed plastics show that on concurrent pyrolysis (copyrolysis) there occur interactions between wood [16] and plastics [18]. The effects of these interactions lead to different composition of the products evolved during the decomposition (Table 5-7).

Compared to the feedstock, the pyroliquid taken from the drip at the end of experiment at 450°C presents a yield of 43.8 %wt.. At 500°C lesser amounts of liquid products evolve (40.4 %wt.) (Table 7). The produced pyroliquid had brown colour and was composed of two layers. These two layers were separated in a separation funnel. The upper layer (oil/hydrocarbon layer) got dissolved in hexane and the bottom layer got dissolved in tert-butanol. The hydrocarbon portion is a mix decomposition hydrocarbons, ranging from C5 to C19, with the strongest representation of C8-aromates (styrene, p-, m-xylene) and straight-chain alkanes and 1-alkenes. The gas-chromatographic composition of the hydrocarbon portion of pyroliquid is rather similar to the composition of the pyroliquid obtained from pyrolysis of only mix plastics [18], the difference is only in the fact that in the pyroliquid that evolves from only plastics there occurs a higher amount of straight-chain alkanes and 1-alkenes.

Concerning the composition of gaseous pyrolytic products, it is obvious that with increasing reaction time and temperature there increases the evolvement of not only low-molecular alkanes, but also alkenes, and conversely, there decreases the production of not only carbon monoxide but also carbon dioxide. From oxides of carbon, carbon monoxide is in prevalence. Out of alkanes, the profiling representation is the one for methane and ethane. Alkenes are significantly represented by propylene and ethylene. The other finding is that in the liquid products the amounts of alkanes and 1-alkenes gradually decreases with growing number of carbon molecule. Starting with pentane, the amount of higher alkanes has been found at tenths of per cent. A growing production of low-molecule alkanes and alkenes on one side and a decrease of production of carbon dioxide on the other side point to the fact that the radicals that are produced in the initiation phase by split reactions can get stabilized by adding some more hydrocarbon atoms (hydrocarbon radicals), which is demonstrated by a considerable production of higher gaseous hydrocarbons. This is true not only for low-molecular alkanes, but also for alkenes (Tables 5 and Table 6).

Table 6 Product distribution (%wt.) of components in gases obtained by thermal cracking of plastics and woody material at 500°C

Temperature, °C Time of experiment, min.	400 24	450 36	500 46	500 116	Average composition of gas
Components, %wt.			Composition, % wt.		
Carbon dioxide	3.0	0.2	0.2	0.2	0.9
Carbon monoxide	90.3	72.6	39.7	18.4	55.3
Methane	1.3	9.4	11.6	13.3	8.9
Ethane	0.3	3.4	8.0	13.4	6.5
Ethylene	0.7	4.6	8.2	12.7	6.5
Propane	0.1	1.7	6.1	8.7	4.2
Propene	0.2	3.7	12.2	16.2	8.1
Methylpropane	tr.	tr.	0.2	0.2	0.1
Butane	tr.	0.5	2.2	3.1	1.5
trans-2-Butene	tr.	0.1	0.7	1.0	0.5
1-Butene	tr.	0.7	2.8	4.5	2.0
Methylpropene	0.1	0.5	1.9	2.1	1.1
cis-2-Butene	tr.	0.1	0.4	0.7	0.3
1,3-Butadiene	tr.	0.2	0.4	0.5	0.3
C_4-hydrocarbons	3.1	0.8	0.4	0.2	1.1
Pentane	0.9	0.8	2.3	0.2	1.6
C_5-hydrocarbons	0.1	0.3	0.6	0.6	0.4
1-Pentene	tr.	0.1	0.6	1.3	0.5
trans-2-Pentene	tr.	tr.	tr.	0.1	0.1
2-Methyl-1-butene	-	0.1	0.2	0.1	0.1
1,3-Pentadiene	-	tr.	0.2	0.2	0.1
2-Methyl-2-butene	-	tr.	0.1	0.1	0.1
Isoprene	-	tr.	tr.	tr.	tr.
Benzene	tr.	tr.	0.2	2.4	tr.

tr. – traces

Certain increase of reaction temperature and prolongation of time are reflected in increased gross calorific value of the produced pyrogas, as a fallow-up of higher presence of alkanes and alkenes, with the interval from 30 to 42 MJ/Nm^3. In a similar dependence also the density of pyrogas rose from 1.2 to 1.27 kg/Nm^3. At 450°C more aromatic hydrocarbons are produced, for example benzene, ethylbenzene, xylene and styrene, than at 500°C (Table 7).

As expected, the liquid products of pyrolysis of only mixed plastics, without wood sawdust particles, contain only hydrocarbons (alkanes, alkenes and aromates). Presence of woody material in the feedstock is demonstrated by production of oxidation products in liquid phase. Because of oxygenated compounds in wood biomass at 47.7 %wt. (Table 3), there occur : methanol, formic acid, acetic acid, lactic acid, furfural, phenol and levoglucosan (Table 7). As has been commented before, the oxidation products are concentrated mainly in the water layer. These oxygenates have been identified as profiling, compared to the existing standards. It is well-known from the literature [19], and from the results of our previous experiments as well, that in the unidenfied portion, that represents 14.6 – 19.4%, there are present some other valuable oxidative substances produced on decomposition of wood biomass.

Table 7 Yields of gaseous and liquids components from thermal cracking of polymer and wood blend at 450^{o}C and 500^{o}C

Temperature, ^{o}C	450	500
Time of experiment, min	103	116
Conversion to gases and liquids, %	0.741	0.811
Components	Yields, %wt.	
Carbon dioxide	1.7	0.4
Carbon monoxide	24.6	22.5
Methane	1.2	3.6
Ethane	0.4	2.6
Ethylene	0.6	2.7
Propane	0.2	1.7
Propylene	0.4	3.3
Butane	0.1	0.6
trans-2-Butene	tr.	0.2
1-Butene	0.1	0.8
Methylpropene	0.1	0.5
1,3-Butadiene	tr.	0.1
2-Methyl-1-butene	-	tr..
1,3-Pentadiene	-	tr.
cis-2-Butene	tr.	0.1
C_4-hydrocarbons	0.6	0.5
Pentane	0.6	0.7
1-Pentene	0.2	0.3
trans-2-Pentene	-	tr.
C_5-hydrocarbons	tr.	0.2
2-Methyl-2-butene	tr.	tr.
Isoprene	tr.	tr.
Benzene	0.8	0.6
1-Hexene	1.0	0.2
1-Heptene	0.7	0.3
Heptane	0.6	0.2
4-Methylheptane	0.1	0.7
1-Octene	0.3	0.3
Octane	0.6	0.2
Ethylbenzene	0.8	0.6
p- + m – Xylene	2.0	1.5
Styrene	2.5	2.3
o-Xylene	0.7	0.5
Nonane	0.4	0.3
1-Decene	0.7	0.6
Decane	0.4	0.4
1-Undecene	0.8	0.8
Undecane	0.5	0.4
1-Dodecene	0.6	0.6
Dodecane	0.5	0.5
1-Tridecene	0.8	0.7
Tridecane	0.4	0.6
1-Tetradecene	0.5	1.0
Tetradecane	0.4	0.8
1-Pentadecene	0.3	0.7
Pentadecane	0.4	0.7
1-Hexadecene	0.1	0.4
Hexadecane	0.3	0.5
1-Heptadecene	0.1	0.3
Heptadecane	0.1	0.4
1-Octadecene	-	0.2
Octadecane	-	0.3
1-Nonadecene	-	0.2
Nonadecane	-	0.2
Methanol	3.9	0.5
Acetic acid	2.6	0.3
Formic acid	1.4	0.5
Furfural	1.5	0.5
Lactic acid	0.4	0.4
Levoglucosane	0.4	1.0
Phenol	1.4	0.2
Nonidentified	14.6	19.4

3. Conclusion

Mixtures of woody material and plastics wastes were thermal cracking with the aim of improving biomass slow pyrolysis by plastics presence. This improvement might be the result of higher heat and mass transfer rates, due to the liquid phase that is more readily formed in the thermal cracking of plastics.

Experimental conditions influenced product yields and composition obtained during thermal cracking of woody material mixed with plastics. The increase of the reaction time between 22 and 116 min caused an increase in the alkane and alkene content of the gas fraction, at the expense of a decrease in the carbon monoxide and carbon dioxide content.

The increase of reaction temperature from 450 to 500°C led to a decrease of the liquid fraction and solid residue and a corresponding increase of the gas and char products. This experimental condition also had a significant influence on the gas composition. At lower temperatures, the formation of carbon monoxide and carbon dioxide was favored, and at higher ones, the alkane formation was higher. Therefore, the increase of gas formation with the temperature and reaction time is mainly due to the higher production of alkanes and alkenes.

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References

[1] Schreirs, Kaminsky, J.W. (Eds): (2006), Feedstock Recycling and Pyrolysis of Waste Plastics : Converting Waste Plastics into Diesel and Other Fuels, John Wiley and Sons, Chichester, pp 785.
[2] Wiliams, P.T.: (2005), Waste Treatment and Disposal, John Wiley and Sons, Chichester, UK, pp 380.
[3] Aguado, J., Serrano,D.: (1999), Feedstock Recycling of Plastic Wastes, The Royal Society of Chemistry, Cambridge, p. 192.
[4] Paradela, F., Pinto, F., Ramos, A.M., Gubyurtlu, I., Cabrita, I.: (2009), J. Anal. Appl. Pyrolysis 85, 392-398.
[5] Hájeková, E., Bajus, M.: (2005), J. Anal. Appl. Pyrolysis 74, 270-281.
[6] Hájeková, E., Mlynková, B., Bajus, M., Špodová, L.: (2007), J. Anal. Appl. Pyrolysis 79, 196-204
[7] Mlynková, B., Hájeková, E., Bajus, M.: (2008), Fuel Processing Technologies, 89, 1047-1055.
[8] Mlynková, B., Bajus, M., Hájeková, E., Kostrab, G., Mravec, D.: (2010), Chemical Papers, 64(1), 15-24.
[9] Bridgwater, A. V.: (2002), Fast Pyrolysis of Biomass : A Handbook, 2, IEA Bioenergy, 2002.
[10] Demirbas, A., Arin, G.: (2002), Energy Sources 24, 471-482.
[11] Karaca, F.: (2006), Energy Fuels 20, 383-387.
[12] Tang, L., Huang, H.: (2005), Energy Fuels 19, 1174-1178.
[13] Onay, O., Kockar, O.M.: (2003), Renewable Energy 28, 2417-2433.
[14] Fogassy, G., Thegarid, N., Toussaint, G., van Veen, A.C., Schuurman, Y., Mirodatos, C.: (2010), Appl. Catalysis B : Environmental 96, 476-485.
[15] Lee, K.H., Nam, K.Y.: (2010), Fuel Processing Technology 91, 514-519.
[16] Bajus, M.: (2010), Petroleum and Coal, 52(3) 207-214.
[17] Mátel, F., Ochocová, R., Findorová, E., Wildová, M.: (2005), Informačný súhrn vybraných faktorov ovplyvňujúcich a podporujúcich rozvoj separácie a recyklácie plastov v SR, Project 1031/04, Nitra 2005.
[18] Bajus, M., Hajeková,E.: (2010), Petroleum and Coal, 52(3) 164-172 (2010).
[19] Müller-Hagedorn, M., H.Bockhorn, H.: (2007), J. Anal. Appl. Pyrolysis 79, 136-146.