Co-pyrolysis of biomass and plastic wastes: investigation of apparent kinetic parameters and stability of pyrolysis oils

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Abstract. This work is dedicated to the co-pyrolysis of real waste high density polyethylene (HDPE) and biomass (rice straw) obtained from agriculture. Mixtures of raw materials were pyrolyzed in their 0%/100%, 30%/70%, 50%/50%, 70%/30%, 100%/0% ratios using a thermograph. The atmosphere was nitrogen, and a constant heating rate was used. Based on weight loss and DTG curves, the apparent reaction kinetic parameters (e.g., activation energy) were calculated using first-order kinetic approach and Arrhenius equation. It was found that decomposition of pure plastic has approximately 280 kJ/mol activation energy, while that of was considerably less in case of biomass. Furthermore, HDPE decomposition takes by one stage, while that of biomass was three stages. The larger amount of raw materials (100 g) were also pyrolyzed in the batch rig at 550 ℃ to obtain products for analysis focussing to their long-term application. Pyrolysis oils were investigated by Fourier transformed infrared spectroscopy and standardized methods, such as density, viscosity, boiling range determination. It was concluded, that higher plastic ratio in raw material had the advantageous effect to the pyrolysis oil long-term application. E.g., the concentration of oxygenated compounds, such as aldehydes, ketones, carboxylic acids or even phenol and its derivate could be significantly decreased, which had an advantageous effect to their corrosion property. Lower average molecular weight, viscosity, and density were measured as a function of plastic content.

1. Introduction

Plastics are unique and widely used materials. The worldwide plastic demand has increased rapidly over recent years, and the production reached the 300 million tons at 2015 [1]. The growth in plastic consumption is also responsible for the increase in municipal solid wastes; therefore the long-term sustainable utilization of plastic and municipal solid wastes is in the focus of waste management. The total municipal solid waste production was around 3.5 billion tonnes in 2015 at Worldwide. Plastic wastes are also responsible for significant environmental problems because they are mainly landfilled and incinerated, which are not to be the sustainable option for long-term waste plastic utilization. On the other hand, plastic waste has high "hidden" energy content. An average municipal plastic waste has a heating value of ~25 MJ/kg, while that of ~15 MJ/kg in case of biomass depending on the composition and water content. It means that significant energy and emissions of greenhouse gases could be saved by their proper recycling. Owing to the extremely slow degradation of plastics, the landfilling needs huge lands, while incinerators have significant exhaust gas emission and needs expensive gas filter unite in the chimney. It is also known, that different plastics should not be blended during the mechanical recycling processes, therefore the selective collection and separation is the weakest point in that recycling. According to report, with less landfill, average incineration, mainly

chemical recycling 70-75MJ/kg waste energy could be saved, while with incineration with energy recovery only 5-10MJ/kg. Regarding CO_2 emission reduction, also the less landfill, average incineration, mainly chemical recycling showed the best option.

The pyrolysis as a process for waste polymer (plastic and biomass) chemical recycling needs high temperatures (400-1000℃) because the raw materials (especially plastics) have low thermal conductivity [2]. The product yields and properties are significantly depended by the reaction parameters; e.g., temperatures, catalysts, raw materials, etc. High pyrolysis temperature favours to increasing in volatile yields, while the catalyst can support the thermal degradation reactions at low temperatures with lower energy consumption [2]-[6]. On the other hand, the cracking reactions are faster leading to less reaction/residence time, furthermore reactor capacity should be smaller using catalysts and higher temperatures [4]. Another important parameter is the raw material because it has a huge impact to the product properties. Non-contaminated hydrocarbons are the products in case of polyethylene, polypropylene and polystyrene pyrolysis, while oxygenated hydrocarbons (aldehydes, ketons, carboxylic acids, phenol and derivates, etc.) could be obtained by biomass pyrolysis [7], [8]. The long-term application of pyrolysis oils are fundamentally affected by contaminates. Chlorine, nitrogen, aldehydes, ketones, carboxylic acids, phenol, and derivates can cause corrosion problems, while the polymerization of unsaturated hydrocarbons leads to storage and transportation problems. Therefore the reductions of before listed components are key for pyrolysis oil long-term application.

It is also well known that the mechanism of thermal degradation of waste plastic is very complex including the following reactions: initiation, propagation, and termination. To understanding the characteristic of waste polymer decomposition it is essential to investigate the reactions leading to volatile products. Numerous papers on waste polymer pyrolysis kinetics have been performed in literature using different reaction kinetic approaches. It can be concluded, that the decomposition reactions are modelled basically as first-order kinetic models and the thermogavimetric method is widely used for analysis connected with coupled techniques, e.g., TG-MS, pyrolysis-TG-MS, etc. [9], [10].

The goal of this work is the investigation of reaction kinetic of real waste HDPE and biomass co-pyrolysis and calculations of apparent reaction kinetic parameters. Pyrolysis was also performed in batch reactor to obtain larger volume of pyrolysis oils, and then the products were characterized focussing to the long-term application regarding their corrosion and transportation properties.

2. Experimental

2.1. Raw material

Mixtures of real plastic waste high density polyethylene (HDPE) and biomass wastes (rice straw) were used as raw material. Both of them were obtained from agriculture sector. Raw materials were milled in a laboratory grinder (Dipre GRS 183A9) into particles up to 0.5 mm. Raw materials were used in their 100%/0%, 70%/30%, 50%/50%, 30%/70% and 0%/100% weight ratio. Table 1 summarizes the main properties of the raw materials.

Table 1. Main properties of raw materials.

	Polyethylene	**Biomass**
Polymer	LDPE, HDPE	Rice husk
Source	agriculture	agriculture
Ash content [a], %	4.1	8.8
Humidity, %	1.02	7.61

[a] combustion in air at 850℃ for 2hours

2.2. TG instrument and calculation

The apparent kinetic parameters of the decomposition reaction and the effects of the raw materials on the pyrolysis were investigated using a MOM DERIVATOGRAPH Q-1500 D type instrument. 200

mg of raw material was weighted in the sample holder and placed in the instrument. Then 20 °C/min heating rate and 40 ml/min nitrogen flow was used for analysis.

The apparent activation energy of the decomposition and pre-exponential parameter were calculated using the Arrhenius equations and first-order kinetic approach:

$$-\frac{dx}{dt} = k \cdot x^n$$

$$k = A_0 \cdot e^{\left(-\frac{E}{RT}\right)}$$

where "E" is the activation energy, "A_0" is the preexponential constant, "m" is the weight of sample, "n" is the reaction order, "k" is the reaction rate coefficient, "t" is the time of degradation, "T" is the temperature and "R" is the universal gas constant. The weight loss fraction of polymer sample was calculated by:

$$x = \frac{m_i - m_t}{m_i - m_f} \cdot 100$$

where "m_i", "m_t" and "m_f" are the initial weight of sample, sample weight at "t" time and final weight of sample, respectively. The weight loss is the function of activation energy, therefore the following equation could be summarized:

$$\frac{dx}{dt} = A_0 \cdot e^{\left(-\frac{E}{RT}\right)}(1 - x)$$

2.3. Pyrolysis in batch reactor

100g of raw materials were also pyrolyzed in an electrically heated batch reactor at 550 °C in nitrogen atmosphere. The reactor temperature was controlled by PID controller. Volatiles from the reactor were condensed and separated into pyrolysis oil and gases in a phase separator (Figure 1). Gases were driven through gas flow meter and a scrubber filled with 1M NaOH dissolution. Condensed fraction was further separated into water and pyrolysis oil in a separator in case of pyrolysis using biomass containing raw material.
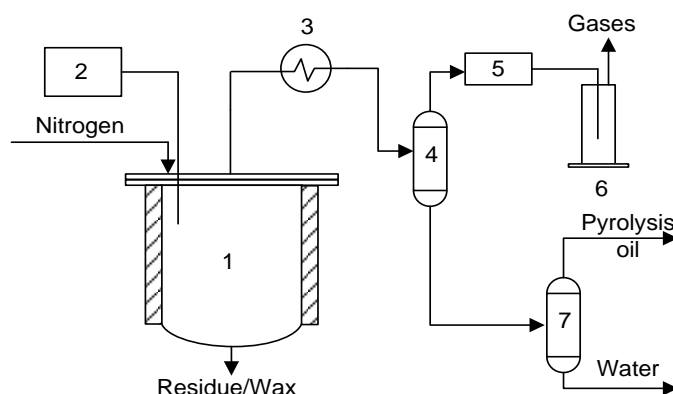

Figure 1. Batch apparatus for plastic/biomass co-pyrolysis (1-Reactor, 2-PID controller, 3-heat exchanger, 4-gas/liquid separator, 5-gas flow meter, 6-scrubber, 7-oil/water separator)

The composition of pyrolysis oil was also analyzed by TENSOR 27 type FTIR-ATR spectrometer in wave-number range of 4000-400 cm^{-1} equipped with an Attenuated Total Reflectance (ATR) accessory (Ge crystal) at room temperature. The uniform number of 32 scans with resolution 3 cm^{-1} was maintained in all case. Pyrolysis oils were also measured by standardized methods.

3. Result and discussion

3.1. Apparent reaction kinetic parameters

The weight loss and DTG curves of pyrolysis are summarized in Figures 2 and 3. Results well demonstrate that significant differences were found among decompositions of raw materials with different plastic/biomass ratio. E.g., biomass sample has three stages decomposition, while HDPE plastic waste has only one.
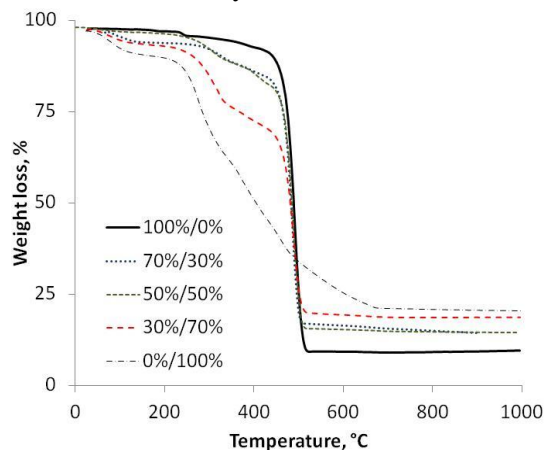

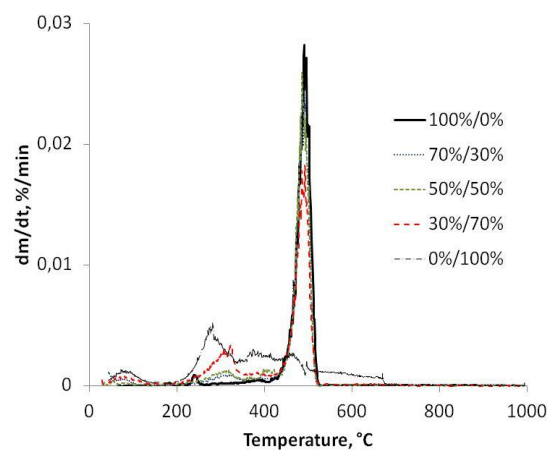**Figure 2.** Weight loss of samples using different polymer/biomass ratio

Figure 3. DTG curves of samples using different polymer/biomass ratio

In 100% biomass and 30%/70% polymer/biomass samples, the first peak around 100 °C can be attributed to their physical dewatering. Biomass sample contain water, which is the reason for 7.61% humidity content. Owing to that, the conversion was between 0.5 and 7% in case of 100% biomass, while 0.5% and 4% in case of 30%/70% polymer/biomass mixture. The drying was finished till 125 °C with peak maximums of 58 (biomass) and 61 °C (polymer/biomass). The calculated activation energies of that stage were 26 and 28 kJ/mol, respectively.

The second stage in diagrams (1st decomposition stage) starts from 1-10% conversion depending on the raw materials and finished at 4-40% conversion. It is also clear, that the conversion range decreased with increasing ratio of HDPE in raw material. E.g., it was 1-4% using 70%/30% polymer/biomass sample or 10-40% in case of biomass. Similar trend was found regarding temperatures (T_i, T_{max} and T_f), which decreased by decreasing biomass content. E.g., the T_{max} was 275 °C using 100% biomass and 262 °C in 70%/30% polymer/biomass ratio. Based on the first-order reaction kinetic approach, the following apparent activation energies could be calculated: 53, 55, 58 and 63kJ/mol in case of 0%/100%, 30%/70%, 50%/50%, 70%/30% and 100%/0% raw materials, respectively. That stage is appears only biomass containing samples and missing in case of HDPE polymer. According to literature, basically the cellulose and hemicellulose are decomposed in that temperature range.

Regarding 0%/100% and 70%/30% polymer/biomass samples, the third stage (2nd decomposition stage) could be attributed to the lignin decomposition. It is important to remark, that decomposition of HDPE also occurs in that range. That stage starts around 350 °C and finished till 506 °C with peak maximum at 455 °C using only biomass sample. It is important observation that the initial temperature increased with increasing HDPE content of the samples, while the T_{max} values were independent from concentration of polymer. On the other hand the T_f values decreased with increasing polymer/biomass ratio. Based on the calculations, it was concluded, that the conversion range was 10-90% regarding 100% HDPE waste with 272kJ/mol activation energy, which could be decreased by biomass. Regarding 70%/30%, 50%/50%, 30%70% and 0%/100% polymer/biomass raw materials, the calculated apparent activation energies were 244, 168, 136 and 62kJ/mol, respectively.

3.2. Pyrolysis oils obtained from batch reactor
Plastic and biomass wastes were also pyrolyzed in batch reactor at 550 °C. The yields of volatiles and the appearance of pyrolysis oils are shown in Figures 4 and 5. Biomass pyrolysis resulted dominant amount of gases (29.5%), while plastic decomposition rather pyrolysis oil (24.2%). However the yield

of volatiles (gases+pyrolysis oil) was significantly higher in case of biomass decomposition. It is important observation that the pyrolysis oil yield was in very narrow range: 24.2-27.6%.

Table 2. Main properties of raw materials.

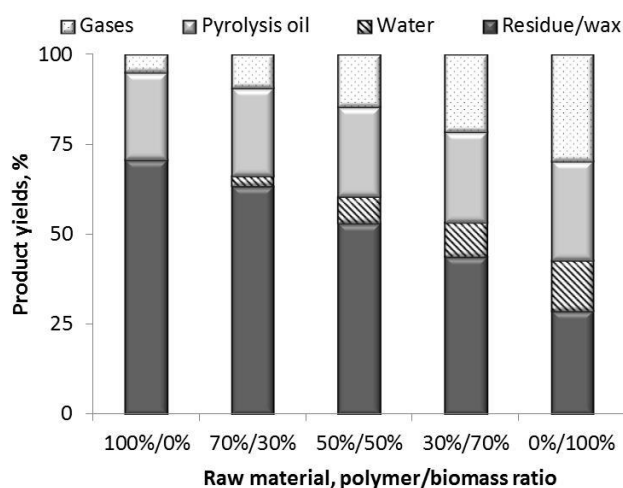|		Polymer/biomass ratio				
		100/0	**70/30**	**50/50**	**30/70**	**0/100**
1st peak	**Conversion, %**	-	-	-	0.5-4	0.5-7
	T_i, ℃	-	-	-	50	50
	T_{max}, ℃	-	-	-	58	61
	T_f, ℃	-	-	-	120	125
	E, kJ/mol	-	-	-	28	26
	A	-	-	-	6.36	6.23
2nd peak	**Conversion, %**	-	1-4	2-6	5-24	10-40
	T_i, ℃	-	172	182	212	222
	T_{max}, ℃	-	262	263	288	275
	T_f, ℃	-	303	307	332	339
	E, kJ/mol	-	63	58	55	53
	A	-	2.65	3.63	3.07	4.54
3rd peak	**Conversion, %**	10-90	15-90	20-95	35-95	45-85
	T_i, ℃	446	450	459	475	346
	T_{max}, ℃	484	483	485	485	455
	T_f, ℃	505	512	515	517	556
	E, kJ/mol	272	244	168	136	62
	A	28.82	25.22	20.44	8.619	10.81

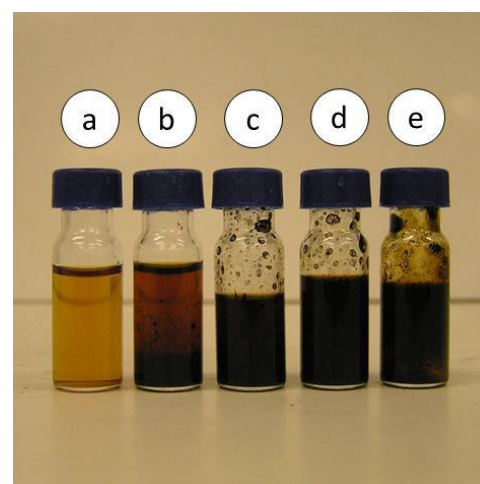**Figure 4.** Product yields using different polymer/biomass ratio (t=60min.)

Figure 5. The appearances of pyrolysis oils (a-100%/0%, b-70%/30%, c-50%/50%, d-30%/70% and e-0%/100%)

Owing to the glycosidic hydroxyl group in cellulose structure, the water yield was also significant in biomass pyrolysis, which was significantly decreased with increasing polymer content of raw materials. Figure 5 well demonstrate that the colour of the pyrolysis oil becomes darker and less transparent with increasing biomass content of raw material.

Pyrolysis oils were characterized as fuel, focussing to the long-term storage and corrosion properties. The FTIR spectra of products are shown in Figure 6. There are well separated intensive signal between 2800 and 3000 cm^{-1}, which are attributed to the symmetric and asymmetric vibration of -CH$_2$-

$((\nu_{as}CH_2, \nu_sCH_2))$ and $-CH_3$ $(\nu_{as}CH_3, \nu_sCH_3)$ groups. Unsaturated hydrocarbons are responsible for bands between 800 and 1000 cm^{-1}: vinyl (910 and 990 cm^{-1}), vinylidene (890 cm^{-1}) and vinylene (960 cm^{-1}). Oil fraction obtained from waste HDPE pyrolysis had intensive signal at 990 cm^{-1}, referring to the dominant $-CH=CH_2$ content, however it was decreased with increasing biomass content. Not only the $-CH=CH_2$ content, but also the concentrations of $-CH_2-$ and $-CH_3$ groups also decreased with increasing biomass/polymer ratio. That is the cause for reduced intensities of infrared signals between 2800 and 3000 cm^{-1}. Regarding vinylidene unsaturated hydrocarbons, more intensive sharp peaks was found using higher biomass content in raw materials. The high concentration of unsaturated hydrocarbons are unflavoured in case of fuel-like utilization of pyrolysis oil, because owing to polymerization of C=C bonds agglomerated macromolecules can be synthetize with less solubility and melting point. That is why they can cause storage and transportation problems. It is well known, that the pyrolysis of biomass resulted alcohols, aldehydes, ketones and carboxylic acids, which are responsible for deteriorations in storage and corrosion properties of pyrolyis oils. Infrared bands between 1140 and 1230 cm^{-1} are caused by phenolic hydrocarbons, which was the most intensive in case of biomass derived pyrolysis oils. Aldehydes (unsaturated, non-conjugated, conjugated, aromatic) resulted infrared bands in 1680-1740 cm^{-1}, however esters also shows infrared activity between 1720 and 1740 cm^{-1} wave number range.
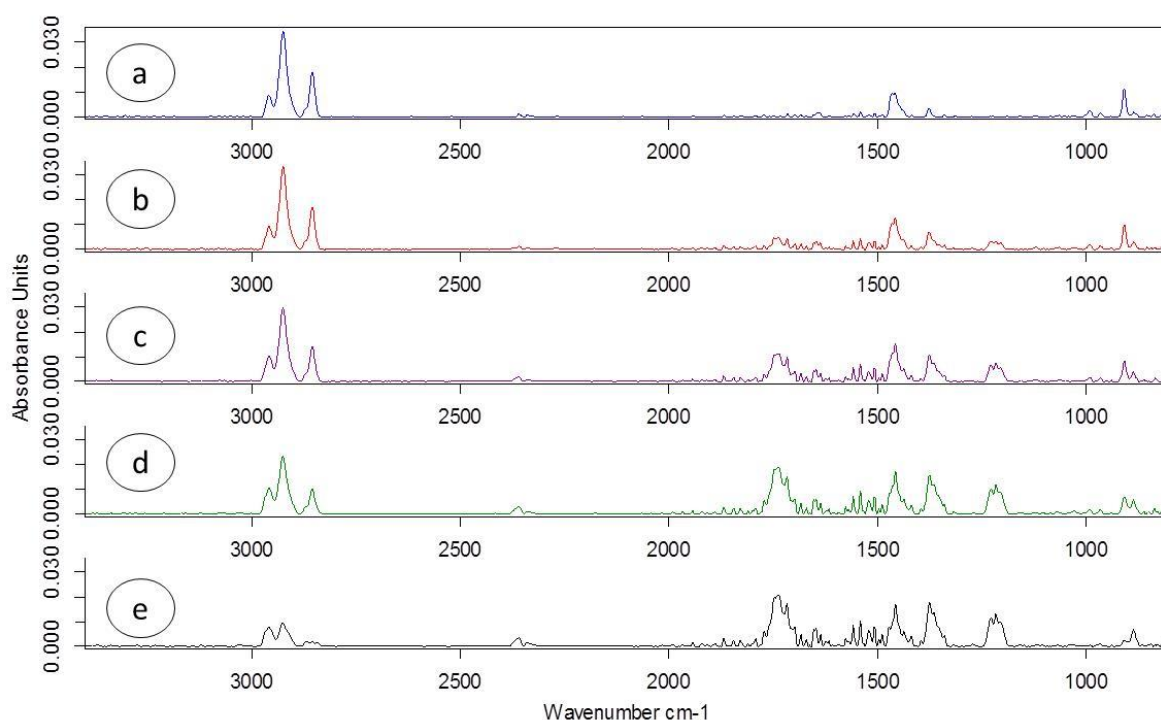

Figure 6. The FTIR spectra of pyrolysis oils
(a-100%/0%, b-70%/30%, c-50%/50%, d-30%/70% and e-0%/100%)

The main properties of pyrolysis oils are summarized in Table 3. Pyrolysis oils have densities of 0.810-0.897 g/cm^3, and kinematic viscosities of 2.1-9.7 mm^2/s. The average molecular weight was between 185 and 195 g/mol. Density, viscosity and average molecular weight are decreased with increasing plastic ratio in raw materials. The result of corrosion test show, that 100% plastic derived pyrolysis oil had excellent corrosion property, while 100% biomass derived had "bad". The quality of pyrolysis oils could be improved by increasing plastic ratio regarding corrosion aspect of plastic/biomass raw materials. Pyrolysis oils had boiling point ranges of 22-341 ℃, which did not changed with raw materials. Plastic derived pyrolysis oil contained saturated and unsaturated hydrocarbons; while biomass derived pyrolysis oil had significant aromatic content.

Table 3. Main properties of pyrolysis oils

	100/0	70/30	50/50	30/70	0/100
Density, g/cm3	0.810	0.828	0.852	0.866	0.897
Viscosity, mm2/s	2.1	3.8	5.5	7.1	9.7
Corrosion test	excellent	good	medium	bad	bad
M, g/mol	185	185	190	190	195
Ash content, %	<0.01	<0.01	<0.01	<0.01	<0.01
Saturated, %	48	46	39	33	29
Unsaturated, %	52	49	45	41	40
Aromatic, %	-	5	16	26	31
Boiling range, ℃	25-334	23-335	24-340	25-332	22-341

4. Summary

In this work the co-pyrolysis of real waste HDPE and rice straw was investigated focussing the reaction kinetic parameters and long-term utilization of products. Based on TG result the apparent kinetic parameters were calculated using first-order kinetic approach. Significant differences were found among the decomposition of raw materials with 100%/0%, 70%/30%, 50%/50%, 30%/70% and 0%/100% plastic/biomass ratio. E.g., biomass decomposition had three stages, while HDPE only one. HDPE pyrolysis needs 272 kJ/mol activation energy, which can be significantly decreased by blending with biomass. Regarding corrosion and transportation stability, biomass derived pyrolysis oil showed non favourable properties, which was improved by plastic in raw material.

5. Acknowledgments

6. References

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