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The effect of clay catalyst on the chemical composition of bio-oil obtained by co-pyrolysis of cellulose and polyethylene

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ABSTRACT

Cellulose/polyethylene (CPE) mixture 3:1, w/w with and without three clay catalysts (K10 – montmorillonite K10, KSF – montmorillonite KSF, B – Bentonite) addition were subjected to pyrolysis at temperatures 400, 450 and 500 °C with heating rate of 100 °C/s to produce bio-oil with high yield. The pyrolytic oil yield was in the range of 41.3–79.5 wt% depending on the temperature, the type and the amount of catalyst. The non-catalytic fast pyrolysis at 500 °C gives the highest yield of bio-oil (79.5 wt%). The higher temperature of catalytic pyrolysis of cellulose/polyethylene mixture the higher yield of bio-oil is. Contrarily, increasing amount of montmorillonite results in significant, almost linear decrease in bio-oil yield followed by a significant increase of gas yield. The addition of clay catalysts to CPE mixture has a various influence on the distribution of bio-oil components. The addition of montmorillonite K10 to cellulose/polyethylene mixture promotes the deepest conversion of polyethylene and cellulose. Additionally, more saturated than unsaturated hydrocarbons are present in resultant bio-oils. The proportion of liquid hydrocarbons is the highest when a montmorillonite K10 is acting as a catalyst.

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1. Introduction

The worldwide organic waste production has continuously grown in the last decades. Nowadays, the effective utilization of organic waste, including plastic, tyres and municipal solid wastes, is being found as one of the major challenges facing the modern world. There is a necessity not only to recycle wastes but also to reduce their volume. As municipal solid waste (MSW) is composed of valuable materials, its recycling is a matter of the highest interest in energy production and the protection of environment. Among, cellulose (cardboard, paper) coexisting with low density polyethylene as aseptic multi-layer packages (Tetra Pak, Combibloc SIG) are important group produced and consumed in large quantities. Therefore, used packages form a significant part of municipal solid wastes. The most common way to recycle used beverage cartons is through recovery of the fiber at paper recycling mills. A part of aseptic cartons is recycled by repulping process with aluminum and polymer being recovered. However according to Tetra Pak International, in many countries there is still no infrastructure for managing household waste usefully, and it is sent to landfill instead. Global recycling of used Tetra Pak cartons increased by 10% in 2012 – from 528 kilo tonnes to 581 kilo tonnes, which is 22.9% of the total (Tetra Laval annual report, 2012).

Pyrolysis treatment has been found to be one of the methods of organic wastes conversion to provide energy and valuable chemicals. The advantage of pyrolysis is that the preliminary MSW sorting is not an essential requirement although it improves the performance of the process. The pyrolysis process is carried out in various types of reactors at different heating rates and final temperature (400–800 °C). All these process parameters influence the yield of gas mixture, bio-oil and solid residue (char or coke).

In literature, plenty of results show the pyrolytic behavior of single materials like biopolymers or synthetic polymers. Nevertheless, there is only a skimp information on the pyrolysis of beverage cartons. However, in view of the co-existence of cellulose and polyethylene in beverage packaging materials, their thermochemical conversion seems to be an attractive way of recycling (Korkmaz et al., 2009; Karagöz et al., 2003; Haydary et al., 2013). In a small number of scientific publications which are available, it has been demonstrated that the co-pyrolysis process could have a potential for the environmentally friendly transformation of lignocellulosic materials and plastic waste to valuable products. The co-pyrolysis of biomass with polyethylene or polypropylene showed that the composition and the nature of both biomass and synthetic polymer as well pyrolysis conditions have a great influence on the yield, the chemical structure and the physical properties of products (Brebu et al., 2010; Sharypov et al., 2002, 2003; Marin et al., 2002; Rutkowski and Kubacki, 2006; Aboulkas et al., 2008; Demirbas, 2004; Jakab et al., 2001, 2000).

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Liquid product of biomass (including MSW) pyrolysis is called bio-oil. It is a mixture of oxygenated organic compounds, and because of its properties is seen as a potential source of chemicals and promising biofuel. Bio-oil is in fact easy to transport, can be directly burned in engines or furnaces to produce energy. It can also be subjected to upgrading processes to obtain more valuable components. However, bio-oil contains a significant amount of water, acidic components and is similar to the elemental composition of the starting material (biomass), which means that it has a number of drawbacks. The main include heterogeneity, corrosiveness, low stability, high viscosity. It requires optimization of biomass conversion process and one of the methods is to use a catalyst to convert the vapors evolving during the thermal decomposition of starting material.

Among many compounds that are formed during the pyrolysis of cellulose, only a few have practical importance including levoglucosan (LG), levoglucosenone (LGO), (1R,5S)-1-hydroxy-3,6-dioxabicyclo[3.2.1] octan-2-one (LAC), 2-furfural (FF) and 5-hydroxymethyl-2-furfural (HMF). The formation of specific compounds during pyrolysis of cellulose is important due to their great potential as the feedstock for fuel and chemicals production (Shen et al., 2013). The aim of many research works was to conduct cellulose pyrolysis process in order to increase productivity of these chemicals (Dobele et al., 2005; Furneaux et al., 1988; Aho et al., 2008; Azeez et al., 2011). Various catalysts based on different zeolites and mesoporous materials, i.e. ZSM-5, HY, MCM-41 were used in the degradation of polyolefins (Serrano et al., 2005; Castano et al., 2011; Aguado et al., 2007). Various natural and synthetic aluminosilicates are widely applied in heterogeneous catalytic reactions and oil conversion processes, as they are solid acid catalysts being efficient towards chemicals and fuels (Dutta, 2012; French and Czernik, 2010). Among solid acid catalysts, commercially available montmorillonite K-10 clay has been shown to contain both Brønsted and Lewis acid sites (Huang et al., 2008). Heating to a higher temperature (200–300 °C) results in a decrease in Brønsted acidity but an increase in Lewis acidity (Kaur and Kishore, 2012). In previous paper, it has been shown that montmorillonite K10 exhibits catalytic activity in levoglucosan conversion during pyrolysis of cellulose (Rutkowski, 2012). It was expected that different clays could be active not only during pyrolysis of cellulose but also during its co-pyrolysis with polyethylene towards liquid fuels.

In this study, authors demonstrate the results of fast co-pyrolysis process of cellulose and low-density polyethylene carried out with and without the addition of clay catalysts. The aim of the research was to develop a catalyst that is suitable for co-pyrolysis of cellulose and polyethylene into liquid fuel with high yield and high contribution of hydrocarbons. The optimization of process temperature and the amount of the best catalyst used is also presented and discussed in the paper.

2. Experimental

2.1. Samples

Commercial microcrystalline cellulose (Cellulose powder, Aldrich) and powdered low density polyethylene were selected for this study. For all processes, cellulose and polyethylene mixture (CPE) in a mass ratio of 3:1 was prepared in a blender. The composition of the CPE blend was selected to be similar to the composition of Tetra Pak type carton packaging. Montmorillonite K10 (K10), montmorillonite KSF (KSF) and Bentonite (B), all supplied by Aldrich, were selected as mesoporous clay catalysts, characterized with different surface area and acidity. All aluminosilicates were thermally pre-treated at 300 °C for 4 h. Characteristics of raw samples and catalysts is given in Table 1.

Table 1

Ultimate and proximate analysis of raw materials (a) and characteristics of clay catalysts (b).

	Cellulose (C)	Polyethylene (PE)	
(a)			
Ultimate analysis			
C^{daf} , wt%	42.51	85.54	
H^{daf} , wt%	6.45	14.21	
N^{daf} , wt%	–	–	
S^{daf} , wt%	–	–	
O (diff), wt%	51.04	0.25	
Proximate analysis			
M_{ad} , wt%	6.9	0.1	
A_d , wt%	0.3	0	
V_{daf} , wt%	92.9	100	
HHV _{ad} , MJ kg ⁻¹	15.2	43.2	
	K10	KSF	Bentonite
(b)			
S_{BET} , m ² /g	235	5	21
V_{total} , cm ³	0.311	0.006	0.041
V_{meso} , cm ³	0.219	0.004	0.031
V_{meso}/V_{total}	70.42	66.67	75.61
V_{DR} , cm ³	0.102	0.003	0.009
L_0 , nm	2.26	2.16	1.71

ad – air-dried sample; d – dry basis; daf – dry ash free basis; diff – calculated by difference.

Elemental composition of initial samples was determined by a CHNS Vario El analyzer (Elemental Analysensysteme GmbH). Oxygen content was calculated by difference. Proximate analysis (moisture – M; ash – A; volatile matter – V; high heating value – HHV) was performed according to the international standards ISO.

The porous texture of aluminosilicates was determined from nitrogen adsorption isotherms measured at 77 K with a NOVA 2200 (Quantachrome). The specific surface area was calculated using the BET method (S_{BET}). The amount of nitrogen adsorbed at relative pressure of $PP_0^{-1} = 0.98$ was employed to determine the total pore volume (V_{total}). The micropore volume (V_{DR}) was calculated applying the Dubinin–Radushkevich equation up to $PP_0^{-1} \leq 0.15$. An average pore diameter (L_0) was also calculated.

Following abbreviation system was used further in the text: **CPE/CAT(a:b)_XXXf** where CAT is a catalyst, (a:b) is the mass ratio (w/w), XXX is a temperature of the pyrolysis process and f is a fast heating. For example CPE/K10(1:1)_450f means mixture of CPE and montmorillonite K10 with a mass ratio of 1:1 (w/w) heated up to 450 °C with a heating rate of 100 °C/s.

2.2. Pyrolysis

The pyrolysis processes of cellulose/polyethylene blend (CPE) with and without catalyst were carried out in a horizontal oven with dynamic heating and cooling systems, as reported previously (Kaur and Kishore, 2012). A 200 mg of CPE mixed with a proper amount of catalyst were placed in quartz reactor and heated up to 400–500 °C with a heating rate of 100 °C/s and kept at final temperature for additional 5 min. The decomposition products were evacuated in nitrogen flow of 10 dm³ h⁻¹ to the liquid reservoir placed in the liquid nitrogen bath. The pyrolysis process was repeated in triplicate to check reproducibility and to calculate an average yield of products.

The yield of solid and liquid products was calculated based on the mass of products (all glass or quartz parts of equipment were weighed before and after pyrolysis process). The yield of char was calculated including aluminum foil. In the case of catalytic processes the mass of catalyst was subtracted from the mass of solid residue. The gaseous product was calculated from the difference according to the following equation: $Y_{gas} = 100 - Y_{char} - Y_{oil}$.

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