Investigation of the features of polyolefins and wood biomass thermochemical conversion for their energy utilization

I G Donskoy, V A Shamanskiy, A N Kozlov, M V Penzik, M A Kozlova
130 Lermontova st., Irkutsk, Russia, 664033
donskoy.chem@mail.ru

Abstract. Combustion of solid combustible wastes is the most common way of their disposal. In developed European countries, up to 50% of all municipal waste is burned; in Russia, it is estimated to be less than 2.5%. The efficiency of modern thermal plants operating on MSW and biomass, as well as the capacity of individual combustion units are continuously increasing, approaching the average values that are close to fossil fuels plants. Replacing coal with combustible waste will make it possible to reduce the cost of energy production and reduce the load on waste landfills. However, to this end, it is necessary to solve the problems of organizing efficient combustion as well as cleaning of combustion products. Of particular interest is the co-processing of municipal waste along with lignocellulosic waste from agriculture and the forest industry. In the present work, the thermal behavior of woody biomass and polyethylene mixtures (in different mass ratios) when heated in an oxidizing environment is investigated using methods of thermal analysis. The distribution of the products of pyrolysis and oxidation is investigated by means of mass spectrometry.

1. Introduction
The problems of municipal waste disposal are urgent. A significant proportion of them are polymeric materials. Production of plastics in the world reaches 300 million tons per year, of which about 40% are packaging materials, which for the most part form waste. Almost 30% of the total production of industrial polymers is polyethylene (PE). In developed countries, in recent years, the specific production of plastic decreases, and the capacity of waste-processing units increases [1, 2]. This is achieved through appropriate environmental legislation and social policies [3]. There are countries importing waste, the international market for waste recycling is continuously developed [1].

Plastic waste can be used by sorting and recycling [4], using thermal decomposition to obtain valuable raw materials (monomers, combustible gases, fuels) [5-7], or by complete combustion producing heat [2]. The choice of technology depends on the content of polymeric materials in the waste and their component composition. Most of the recyclable municipal waste is currently utilized by combustion.

Thermochemical conversion of polymers faces a number of problems, primarily, the cleaning of thermal decomposition gases to prevent the emission of halogens and polyaromatic compounds. The addition of chlorine-containing polymers affects the evaporation of mineral components [8]. The formation of a significant amount of liquid products can be both a positive and a negative circumstance, depending on the target products of processing.

The development of new efficient methods for processing plastics requires the study of the physicochemical features of their thermochemical transformations [9, 10]. The polymers have a high calorific value, but their complex thermal behavior (melting, endothermic destruction, swelling [11])
leads to difficulties in combustion associated with the mechanical stability of materials and the unpredictable composition and complex chemical behavior of thermal decomposition products [12, 13]. Therefore, the most common reactors for thermochemical conversion of polymers are rotary kilns and augers, and the processes are carried out in allothermic and staged modes [14-17], including post-conversion of liquid tarry products [18, 19]. Promising ways to recycle waste are plasma and catalytic processing [20, 21].

Gasification and incineration of polymeric waste often require the addition of higher-grade fuel. For example, biomass can be used, which is usually also a waste. It has better mechanical and reactive properties, but less calorific value. Their co-conversion in some cases is more effective than separate processing [21].

Gasification and combustion can be carried out in fluidized bed reactors [22-24] (including those with two-stage reactors [25-28]) and in the fixed-bed reactors [29-31]. In the works on thermochemical conversion of mixtures of biomass and polymers, sintering and clinkering problems are often noted, which are associated both with sticking of particles due to the adhesive properties of pyroliquid [32], and because of a temperature increase in the combustion core leading to melting of ash [33]. In this regard, the proportion of plastic in the fuel mixture is often limited [13, 34].

Thermal oxidation of polyolefins proceeds through the radical reactions concerned with peroxide compounds [35], so plastic decomposition in an oxidizing environment begins at lower temperatures compared to pyrolysis [36]. Measurements (for example, carried out in [37]) show that the set of oxidation products is very diverse. These are mainly hydrocarbons, alcohols, aldehydes and ketones, the number of carbon atoms in molecules of products can reach 20 or more units. Aromatics may form at high temperatures [38]. Wood contains a significant amount of oxygen, so its thermal destruction begins at lower temperatures compared to plastics. Composition and particle size of polyolefin and wood could significantly affect the kinetics mixture decomposition due to averaging of thermophysical properties, reaction chains interaction and interfacial phenomena [39-41].

2. Experimental study

In this work, thermal decomposition of wood biomass and low pressure PE was studied at different mass ratios when heated at a rate of 30°C/min in an oxidizing environment using the complex thermal analysis unit STA449F1 combined with the QMS403C quadrupole mass spectrometer. Calibrated pine sawdust (lignin content 29.6% wt., tar content 4.4% wt.) with a size of 0.6-1.0 mm, and particles of PE with a size ~1 mm were used as raw materials. Mixtures with PE content ranging from 0 to 100% wt. were investigated with increments of 20%. The environment gas mixture was formed from 10 ml/min of argon and 70 ml/min of air and was fed into the analyzer's heat chamber. The obtained thermogravimetric and DSC curves are shown at Fig.1. First curve at Fig. 1a corresponding to a sample consisting of pure wood (0% PE) has a characteristic section, where it is possible to distinguish intervals with sequential decomposition of cellulose and lignin components of wood. The final section of the curve corresponds to the oxidation of char, which is formed during oxidative pyrolysis. For a pure PE sample, the rate of mass loss monotonously increases, and thermogravimetric curve has no characteristic sections. That indicates that in the process of oxidative pyrolysis of pure PE char is not formed.
Fig. 1. TG-curves (a) and DSC-signal (b) measured during oxidation of wood and PE (legend shows PE content).

Fig. 2. Differences between actual and additive thermal behaviour of samples (legend shows PE content).

The main effect that is expected from the thermal co-conversion of various organic polymers is the mutual influence on the rate and products of decomposition. Fig. 2b shows deviation curves obtained as the difference between actual thermogravimetric curves and additive curves calculated for present mixture compositions. One can see two weak positive peaks in the vicinity of temperatures of 630 and 820 K, which are the higher the greater the amount of PE in the mixture, and a significant negative peak in the region of 720–750 K.

The first two peaks occur in areas of the most rapid burning of wood, so it can be concluded that the presence of PE to a small extent contributes to the oxidation of both the carbohydrate components of the wood and the char conversion. In this case, the pure PE in the region of ~620 K is slightly oxidized, which is also confirmed by the relatively small value of the DSC signal at this temperature for pure PE (Fig. 1b). At the same time, in the 820 K zone, the deviation from the additivity of the DSC signal is considerable and positive, and when the content of PE in the mixture exceeds 20%, the difference does not grow significantly (Fig. 2b). This indicates that the char conversion rate and the PE molecules destruction rate both increase, and decomposition products also could react in the area above the sample.

Figure 1b also shows that in this temperature range, for pure PE, noticeable endothermic processes take place, which, apparently, is connected with the thermal destruction of the hydrocarbon polymer. Thus, the char particles, whose surface is covered with molten products of incomplete decomposition of PE, during combustion could contribute both to the acceleration of the endothermic destruction of hydrocarbon chains and their partial oxidation.

The region of negative deviations of the measured mass of mixtures from additivity (Fig. 2a) indicates a significant decrease in the overall burning rate as a result of the mutual influence of the components. For samples with a PE content of more than 60%, the total thermal effect of oxidative thermal conversion at temperatures of 850–950 K drops to the region of the endothermic process, which is certainly due to the predominance of PE in the mixture and incomplete oxidation of
thermolysis products. Figure 3 shows the mass spectra of the products of thermal-oxidative decomposition of the studied mixtures.

As expected, the main products of oxidation are carbon dioxide and water. Moreover, they are practically the only ones for mixtures up to 20% PE content. When the content of PE is 40% and higher, an increase in the amount of incomplete oxidation products appears. It is extremely difficult to analyze the composition of these products. For the case of pure PE, starting with a mass number of 50, mass spectra signals appear on almost every mass number up to 150. As the amount of wood increases, “gaps” appear between the mass numbers. According to the experimental conditions, the actual amount of oxygen in the thermoanalyzer chamber is much higher than stoichiometric; therefore, high content of oxidized products leaving the reaction space (in the case of pure PE) indicates first of all the existence of kinetic restrictions obstructing complete oxidation. Since the development of the combustion process proceeds by a radical mechanism, it is reasonable to assume that in the case of thermal decomposition of PE, the resulting hydrocarbon radicals terminate the development of the oxidation process, in which the OH, H and HO₂ radicals play a role in the formation of alcohols, aldehydes and carboxylic acids (similar to inhibiting pyrolysis process in [42]). Since the mass numbers corresponding to the hydroxyl (OH), methoxy (CH₃O) and carboxyl (COOH) groups overlap with more intense peaks of water, oxygen and carbon dioxide, respectively, this fact can be observed most clearly at ion currents corresponding to a m/z = 29 (aldehyde group, CHO), shown at Fig. 4.
Fig. 4. Ion currents obtained for m/z = 29 and 44 of pure PE and wood-PE mixtures.

It can be seen from the figure that with an increase in PE fraction, the peak values of the ion currents grow (as well as their areas). In the case of PE content in a mixture is 20% and below, the aldehyde peaks in the mass spectra are not observed (Fig. 3). Comprehensive analysis of the oxidation kinetics is beyond the scope of this article, but it should be noted that the increase in the yield of aliphatic aldehydes decreases within the temperature range, where an increase in the mixture burnout rate (Fig. 1a) and the exothermic deviation of the DSC signal from additivity (Fig. 2b) are observed. This indicates that in this temperature region the presence of wood prevents the formation of oxygenates polymeric hydrocarbon molecules. Figure 4 shows also the ion currents of carbon dioxide mass spectra, from which it is clear that even a small amount of wood in the system reduces the formation of aliphatic aldehydes in the combustion products towards complete oxidation of organic carbon. Perhaps this is explained by the decomposition and oxidation of lignin components taking place in the same interval in the case of pure wood (Fig. 1). Heat release during their oxidation contributes to the development of deeper oxidation processes of hydrocarbon fragments produced by the degradation of PE. As for the peak on the aldehyde mass spectra corresponding to pure PE and the decrease in its area during carbon dioxide formation, both of these circumstances indicate an increase in the decay rate of carbon chains, and a slight decrease in the oxidation rate of the terminal carbon atoms in polymer molecules, which contributes to the formation of carbon dioxide.

Conclusions
The processes of combined oxidative thermopyrolysis of wood and PE have a significant non-additive effects, both due to a change in the chemical mechanism of the processes taking place and due to the interaction of dissimilar thermal and kinetic effects. In our opinion, processes of initiation and inhibition of radical chemical reactions in the gas phase and at the surface of particles covered by the molten plastic play important role.

When the content of PE is 40% and higher, products of incomplete oxidation are intensively emitted, and in order to eliminate them, it is necessary to organize an additional oxidation zone. The optimal consumption of wood, PE and gas, as well as the geometry of the secondary reaction space needs to be studied using detailed kinetic and hydrodynamic models.

One of the problems of plastic-rich waste incineration is swelling and agglomeration of particles, which are associated with the formation of high-adhesive liquid substances [51]. In this regard, it is interesting to search for conditions in which the yield of such products is minimal. The results of the study show that, with a plastic fraction of 20% and below, no essential formation of long hydrocarbons and oxygenates are observed. However, the local fraction of plastic may be high enough due to incomplete mixing of raw materials and due to the heterogeneity of such systems: the interaction between biomass and plastic particles occurs at the interface, where the proportions of the components are comparable even with a low gross fraction of plastic. Therefore, in addition to the physicochemical
characteristics of the conversion of mixtures, it is necessary to investigate the behavior of particles under fixed bed conditions.

Acknowledgements
This work was supported by the Russian Fund for Basic Research (project number 19-08-00744) and was carried out using equipment of the multi-access scientific center "High Temperature Circuit".

References
[1] Malinauskaite J, Jouhara H, Czajczynska D, et al. 2017 Energy 141 2013
[2] Castaldi M, van Deventer J, Lavoie JM, et al. 2017 Waste Biomass Valor. 8 1875
[3] Mwanza BG and Mbohwa C 2017 Procedia Manufacturing 8 649
[4] Singh N, Hui D, Singh R, et al. 2017 Composites Part B: Eng. 115 409
[5] Arena U 2012 Waste Manag. 32 625
[6] Wong SL, Ngadi N, Abdullah TAT and Inuwa IM 2015 Renew. Sust. Energy Rev. 50 1167
[7] Ardolino F, Lodato C, Astrup TF and Arena U 2018 Energy 165B 299
[8] Zhang Z, Liu J, Shen F, Zhang Z and Dong Y 2018 Fuel 221 249
[9] Horton SR, Zhang Y, Mohr R, Petrocelli F and Klein MT 2016 Energy Fuels 30 7904
[10] Ranzi E, Faravelli T and Manenti F 2016 Adv. Chem. Eng. 49 1
[11] Zhou C, Zhang Q, Arnold L, Yang W and Blasiak W 2013 App. Energy 107 173
[12] Salganskaya MV, Glazov SV, Salganskii EA and Zholudev AF 2010 Russ. J. Phys. Chem. B. 4 928
[13] Donskoi IG 2018 Solid Fuel Chem. 52 121
[14] Malkow T 2004 Waste Manag. 24 53
[15] Alvarez J, Kumagai S, Wu C, et al. 2014 Int. J. Hydrogen Energy 39 10883
[16] Chen D, Yin L, Wang H and He P Waste Manag. 2014 34 2466
[17] Sipra AT, Gao N and Sarwar H 2018 Fuel Proc. Tech. 175 131
[18] Ohmukai Y, Hasegawa I and Mae K 2008 Fuel 87 3105
[19] Jin Q, Wang X, Li S, et al. 2019 J. Energy Inst. 92 108
[20] Al-Salem SM, Antelava A, Constantinou A, et al. 2017 J. Env. Manag. 197 177
[21] Lopez G, Artetxe M, Amutio M, et al. 2018 Renew. Sust. Energy Rev. 82-1 576
[22] Ephraim A, Minh DP, Lebonnois D, et al. A 2018 Fuel 231 110
[23] Van Kasteren JMN 2006 J. Mater. Cycles Waste Manag. 8 95
[24] Mastelone ML, Zaccariello L, Santoro D and Arena U 2012 Waste Manag. 32 733
[25] Narobe M, Golob J, Klinar D, et al. 2014 Biomes. Tech. 162 21
[26] Cho M-H, Mun T-Y, Choi Y-K and Kim J-S 2014 Energy 70 128
[27] Robinson T, Bronson B, Gogolek P and Mehrani P 2016 Fuel 178 263
[28] Lin C-L and Weng W-C 2017 Renew. Energy 109 135
[29] Nunes SM, Paterson N, Herod AA, et al. 2008 Energy Fuels 22 1955
[30] Garcia-Bacaioca P, Mastral JF, Ceamanos J, et al. 2008 Biomes. Tech. 99 5485
[31] Vonk G, Piriou B, Dos Santos PF, et al. 2019 Waste Manag. 85 106
[32] Ouadi M, Brammer JG, Kay M and Hormung A 2013 App. Energy 103 692
[33] Madadian E, Crowe C and Lefsrud M 2017 J. Cleaner Prod. 164 137
[34] Couto ND, Silva VB and Rouboa A 2016 J. Cleaner Prod. 139 622
[35] Iring M and Tudos F 1990 Prog. Polymer Sci. 15 217
[36] Peterson JD, Vyazovkin S and Wight CA 2001 Macromolecular Chem. Phys. 202 775
[37] Bravo A and Hotchkiss JH 1993 J. App. Polymer Sci. 47 1741
[38] Goncalves CK, Tenorio JAS, Levendis YA and Carlson JB 2008 Energy Fuels 22 372
[39] Oyedun AO, Gebreegziabher T and Hui CW 2013 Chem. Eng. Trans. 35 883
[40] Sophonrat N and Yang W 2017 Energy Procedia 142 315
[41] Xiong S, Zhuo J, Zhou H, et al. 2015 J. Analyt. App. Pyrolysis 112 66
[42] Kumagai S, Fujita K, Kameda T and Yoshioka T 2016 J. Analyt. App. Pyrolysis 122 531