Thermal decomposition of polyethylene agglomerates in a porous medium

I G Donskoy1, D A Svishchev1, A N Kozlov1 and M V Penzik1

1Melentiev Energy Systems Institute of SB RAS, 130 Lermontov st., Irkutsk, Russia
donskoy.chem@mail.ru

Abstract. Fixed-bed combustion of compositions with polymeric materials (for example, municipal solid waste) is often difficult due to the agglomeration phenomenon: when heated, the waste particles swell and emit a significant amount of viscous products, resulting in formation of clumps of particles that have low air permeability. Using experimental and theoretical models, some features of the formation and decomposition of agglomerates are investigated. Samples of the agglomerates were prepared in a laboratory batch unit by heating a mixture of polyethylene granules and clay particles. Using a mathematical model, numerical calculations of the heating regimes were performed under the conditions of an experimental unit. A change in the shape of the agglomerate at different points in time is considered.

1. Introduction

The problems of thermal utilization of municipal solid waste are associated with low efficiency of its burning. A high proportion of noncombustible components, moisture, mechanical instability of the bed leads to high underburning and the formation of harmful substances. In previous papers [1, 2], limitations on the efficiency of combustion and gasification processes related to agglomeration of fuel particles were discussed. To solve these problems (including the development of methods for predicting agglomeration), it is necessary to study thermophysical processes in the reacting layer in more detail. Models of sintering of particles in a fluidized bed were proposed in [3, 4], but there is not much work on the study of sintering in a fixed bed combustion. However, there are the papers [5, 6] related to the study of changes in the bed porosity during combustion.

Polymeric materials are main components of the municipal waste. Their thermal decomposition and burning can lead to a local decrease in the permeability of the bed, due to softening and melting of plastic at the heating stage, as well as softening and melting of the mineral part at the intensive burning stage [7-9]. Both mechanisms are similar to each other. Due to the heterogeneity of the temperature distribution in the bed, agglomerates can form. Agglomeration leads to a decrease in the combustion rate, to the formation of underburning and blocking of the fixed bed.

In the present work, the following agglomeration mechanism is considered: the formation of agglomerates is associated with the softening of plastic mass, which fills the porous space, which leads to a shortage of gaseous oxidizing agent in a small region of the layer, worsening burn-out, lowering temperature, and the growth of stagnant sections with reduced permeability (such areas were observed in experimental work [10]). To study these processes, mathematical model [11] of transport processes in porous media in a two-dimensional setting is used. Similar mathematical models were proposed in [12] for waste incineration process and in papers [13, 14] for studying the thermal regimes of reacting porous media.
2. Experimental section

Samples of the agglomerates were prepared in a laboratory unit (internal diameter of 15 cm, bed height of 14 cm) by heating a mixture of polyethylene granules and ceramic particles (mass ratio of 1:1, bed weight is 600 g, mean particle size is 5 mm). The scheme of the unit is shown in Figure 1. The walls of the reactor are heated by an electric spiral to a temperature of 350-400°C. The bed is purged with argon (2 l/min) to prevent ignition. During heating, the polyethylene melts and fills the porous space, resulting in bed shrinking. In these experiments, polyethylene is distributed uniformly in bed, and the size of the agglomerate is determined by the size of the unit, although a decrease in the polyethylene content is observed near the walls, which is associated with better conditions for the melt to drain. The resulting agglomerates are then subjected to air oxidation (flow rate of 25 l/min) in the same unit with heating of the walls up to 700°C.

![Experimental unit](image)

**Figure 1.** Experimental unit.

The temperature increase during decomposition of the agglomerate is shown in Figure 2. Thermocouples Nos. 1-3 are located in the bed at the bottom, half-height and upper boundary (2 cm from the wall), thermocouple No. 4 is located at the gas outlet from the unit (this zone has no thermal insulation, so its temperature is lower than bed temperature). Decomposition of the agglomerate occurs on its surface, and most of the mass is not involved in the reaction. Combustion occurs quite slowly due to melting and deformation of the surface. Therefore, despite a significant external supply of heat, intensive combustion is observed only at the latest stage of experiment. Pressure drop rises at the beginning of experiment due to heating and melting of bed material, but after start of polyethylene decomposition it gradually decreases. After the temperature and pressure drop are stabilized, the heating was turned off. Inspection of the contents showed that the decomposition of polyethylene was quite complete: ceramic particles restored permeability completely, no polymer residues were found on the walls and at the bottom after removing the material from the unit.

![Experimental data](image)

**Figure 2.** Experimental data on agglomerate decomposition: (a) temperature measurements, (b) pressure drop measurements.
3. Theoretical section

With the help of the mathematical model, developed in [11], numerical calculations of the heating parameters in the experimental setup were carried out. This model includes two-dimensional non-stationary equations of heat and mass transfer in a porous medium. The temperature and pressure fields in the reactor have cylindrical symmetry. Gas moves according to Darcy law, but local values of permeability and porosity depend on the mass concentration of polyethylene. The permeability and porosity of the agglomerate are small, however, when the polymer decomposes, their values increase significantly (by 1-2 orders of magnitude). The initial distribution of the polymer mass is uniform over the layer, but there is no polyethylene in the narrow near-wall region. The decomposition of polyethylene is considered as one-stage reaction, the effective kinetic coefficients of the decomposition are taken from [15]. A comparison of experimental and calculated temperatures is shown in Figure 3.

![Figure 3. Temperature in the bed: (1) half-height of bed, (2) upper boundary of bed.](image)

The distribution of polyethylene in the layer was not experimentally measured. The calculated form of agglomerate at different points in time is determined by the isolines of the polyethylene mass fraction (see Figure 4). The decomposition of polyethylene begins at temperatures of the order of 400-500°C, mainly in the near-wall region of the bed (this temperature range corresponds to pressure peak in Figure 2). The front of the thermochemical transformation moves to the center of the bed, and the agglomerate decreases in size in all directions.

Figure 5 shows the results of calculations on the decomposition of agglomerate with different wall heating rates of up to 700°C. The agglomerate decomposition rate does not depend on the heating rate and is apparently determined by the thermal conductivity of the bed material. The heating rate determines the delay time for the start of decomposition.
Figure 4. Change in the size and shape of the agglomerate over time during its heating and decomposition according to the results of mathematical modeling: on the level lines, the fraction of polyethylene, \( Y \) – granular bed radius, \( Z \) – granular bed height.

Figure 5. Overall decomposition of polyethylene in bed under different heating rates (values are presented in the legend, K/s).

The burning of the agglomerate with a diameter of about 15 cm under laboratory conditions (with external heating) took about 1 hour. Under the conditions of fixed bed furnaces and gasifiers, this time can be longer, since the possibilities for heating the air are usually limited, and the agglomerates can be larger. In further works, we will study the agglomeration features in mixtures of polymers with other grades of fuel, such as coal and wood waste.

**Conclusion**

Using a laboratory installation for fixed bed combustion, samples of polyethylene agglomerates with inert filler (ceramic clay) were obtained. The resulting samples were oxidized by air with external heating of up to 700°C. Using the developed mathematical model, the observed features of the decomposition of the agglomerate were reproduced. The influence of the wall heating rate on the decomposition of the agglomerate is estimated.
Acknowledgments
The reported study was funded by RFBR according to the research project № 19-08-00774. Equipment of the multi-access scientific center "High Temperature Circuit" was used in this study.

References
[1] Donskoi IG 2018 Solid Fuel Chem 52 121. DOI: 10.3103/S0361521918020027
[2] Donskoy IG 2019 E3S Web Conf 114 06006. DOI: 10.1051/e3sconf/201911406006
[3] Khadilkar A, Rozelle PL, Pisupati SV 2014 Powder Tech 264 216. DOI: 10.1016/j.powtec.2014.04.063
[4] Morris JD, Daood SS, Chilton S, Nimmo W 2018 Fuel 230 452. DOI: 10.1016/j.fuel.2018.04.098
[5] Duffy NTM, Eaton JA 2013 Combust Flame 160 2204. DOI: 10.1016/j.combustflame.2013.04.015
[6] Duffy NTM, Eaton JA 2016 Combust Flame 167 422. DOI: 10.1016/j.combustflame.2015.12.032
[7] Madadian E 2018 Gasification for Low-Grade Feedstock. (InTech.) p. 79. DOI: 10.5772/intechopen.77119
[8] Salganskaya MV, Glazov SV, Salganskii EA, Zholudev AF 2010 Russ J Phys Chem B 4 928. DOI: 10.1134/S1990793110060096
[9] Tsvetkov MV, Zyzkin IV, Freiman VM, Salganskaya MV, Tsvetkova YY 2017 Russ J Appl Chem 90 1706. DOI: 10.1134/S1070427217100226
[10] Allesina G, Pedrazzi S, Tartarini P 2013 Bioreas Tech 146 704. DOI: 10.1016/j.biortech.2013.07.132
[11] Donskoy IG 2020 Computational Technologies 25(4) 22. DOI: 10.25743/ICT.2020.25.2.003
[12] Yang YB, Swithenbank J 2008 Waste Manag 28 1290. DOI: 10.1016/j.wasman.2007.04.012
[13] Lutsenko NA 2018 Combust Theor Model 22 359. DOI: 10.1080/13647830.2017.1406617
[14] Lutsenko NA, Fetsov SS 2019 Int J Comp Meth 16 1950010. DOI: 10.1142/S0219876219500105
[15] Bockhorn H, Hornung A, Hornung U, Schawaller D 1999 J Analyt Appl Pyr 48 93. DOI: 10.1016/S0165-2370(98)00131-4