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Simplified dynamic simulation model of plastic waste pyrolysis in laboratory and pilot scale tubular reactor

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ABSTRACT

Thermal pyrolysis of plastic wastes in tubular reactor has been studied with Direct Computer Mapping based simulation methodology, combined with genetic algorithm. Degradation process was carried out in laboratory and pilot scale tubular reactor. The investigated pyrolysis temperature range was 465–545 °C, and raw material feeding rate was between 6 and 20 g/min. A dynamic simulation model has been developed based on a four-step degradation scheme, considering four cracking product fractions (gas, naphtha, middle distillate and heavy oil) and their hydrocarbon composition (paraffin, olefin and aromatic). A collaborating genetic algorithm was used for the identification of kinetic and stoichiometric model parameters. Having analyzed the identification results we concluded that some of the stoichiometric parameters, moreover all of the kinetic parameters and vapour/liquid phase ratios were independent from the reaction parameters, however they depend on the quality of raw material. The temperature and feeding rate dependency of the model were considered by two calculated parameters (pLiq, pAro). According to the investigations, the rate determining factor of the degradation process is the effectively utilized enthalpy resulting from the heat transfer through the wall of the equipment. The simplified dynamic simulation model can support the scale-up procedure of the pyrolysis technology.

1. Introduction

Owing to the continuous innovation, plastic production is increasing significantly. The total global production of plastics has grown from around 1.3 million tons in 1950 to 320 million tons in 2010. Obviously, the generation of waste from plastics is also increasing. Increasing cost and decreasing space of landfills are forcing considerations of alternative options for plastic waste disposal. Number of treatment, recycling and recovery methods have been developed for plastic waste that can be economically and environmentally viable. Recently, much attention has been paid to chemical recycling (mainly thermal and thermo-catalytic pyrolysis) as a possible method of plastic waste recycling [1–12]. In pyrolysis plastic waste was converted into various hydrocarbon fractions (gas, naphtha, gas oil etc.). For pyrolysis different reactors have been developed: batch, fluid-bed, tubular, semi-continuous, etc. The reactor type is one of the major elements of the cracking technology, because large amount of heat should be transferred through the reactor wall to ensure the heat of polymer degradation. It is important to remark that pyrolysis experiments were dominantly operated at laboratory conditions. Only limited information is available about the larger scale processes, but many countries are developing processes for waste polymer pyrolysis [1–14]. The description of the decomposition reactions is important for further development and product optimization. There are many parameters which have a great influence on the product yields and quality: temperature, residence time, catalysts, etc. Regarding the cracking reactions the heat transfer is the key parameter. The heat transfer is not an investigated parameter in case of laboratory processes, but in case of industrial scale equipment, the heat and component transfer should be considered together. Furthermore, knowing of transport processes in the pyrolysis reactor, it is necessary for the further design, optimization and scale-up procedure. This would lead to the development of models which simulate the degradation of plastics in cracking reactors. Generally first order kinetic approach is used for cracking reaction modeling. On the other hand, the batch reactors are dominant in pyrolysis experiments, the thermogravimetric analysis connected with different techniques (e.g. TG, DTG, DSC, TG–MS, DTG–MS etc.) is predominant [17–22,31]. Owing to the difficulties, caused by the geometry of the reactor and great amounts of materials (e.g. circulation, heat transfer, coking, fouling etc.), only limited kinetic information is available for continuous or semi-continuous conditions [23–26]. In our earlier work the reaction kinetic approaches for waste polymer pyrolysis

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have been summarized [32–36]. It was concluded that the commonly used approach is the first order kinetics to investigate the characteristics of degradation, completed with the Arrhenius equation (Eqs. (1) and (2)).

$$-\frac{dm}{dt} = k \cdot m^{n}, \quad t = 0 \rightarrow m = m_0 \tag{1}$$

$$k = A_0 e^{\frac{E}{RT}}. \tag{2}$$

Where m_0 is the weight of sample, n is the reaction order, k is the reaction rate coefficient, m is the weight of residue, t is the time of degradation, E is the activation energy and A_0 is the preexponential constant. Relations might become simple by using of thermogravimetric and different connected methods, but the heating rate as a new parameter is to be introduced. The approaches for the determination of kinetic parameters based on thermogravimetric data are among others Flynn–Wall, Friedmann, Kissinger, Ozarawa or Horowitz–Metger methods [27–29]. Flynn–Wall, Horowitz–Metger and Friedmann gave excellent correlation in case of polypropylene pyrolysis [28,29]. In case of the catalytic pyrolysis, the catalyst deactivation as function of reaction time is another key parameter. The problem is that the activation energy decreasing effect of the catalyst changes in time. That is why the first order kinetics should be used only with serious simplifications in thermo-catalytic pyrolysis and another equation is proposed for fluid catalytic cracking, that takes into consideration the catalyst deactivation in refineries [30], as follows:

$$\eta = \exp[-\alpha C(c)] \tag{3}$$

where η is the loss of catalyst activation, C(c) is the coking of catalyst and α is a constant depending on the type of catalyst. It is clear that it must be calculated η for each catalyst.

For software supported kinetic parameter calculation (especially reaction rate constant) the MATLAB Simulink was also applied. It is important to remark that those models are based on the first order kinetic approach, too. Moreover, key parameters were calculated, based on the data, obtained from thermogravimetric apparatus directly [17–22]. Elordi et al. investigated the adaptability of nine proposed degradation kinetic schemes to the fast pyrolysis process of high density polyethylene in conical reactor at different temperatures (450–715 °C) [8]. The formation of product fractions was calculated by the kinetic equations of the given reaction scheme. The equation systems were solved by a program written in MATLAB. According to the calculated and experimental results the best models (Fig. 1) were determined, where polyethylene degrades in three steps to gas, liquid and wax fractions and the secondary reactions give liquid and aromatics which resulted char.

There are exact and detailed kinetic models about the thermal decomposition of various polymers [2–28]. Levine et al. have created a detailed, mechanistic model for pyrolysis of various polymers based on the method of moments and it was used to study the time evolution of the formed low molecular weight hydrocarbon products [3,4]. The role of various reaction pathways (unzipping, backbiting and random scission) of polymer degradation was studied in the evolution of low carbon number (C_{1-23}) alkane and alkene species. Mastral et al.

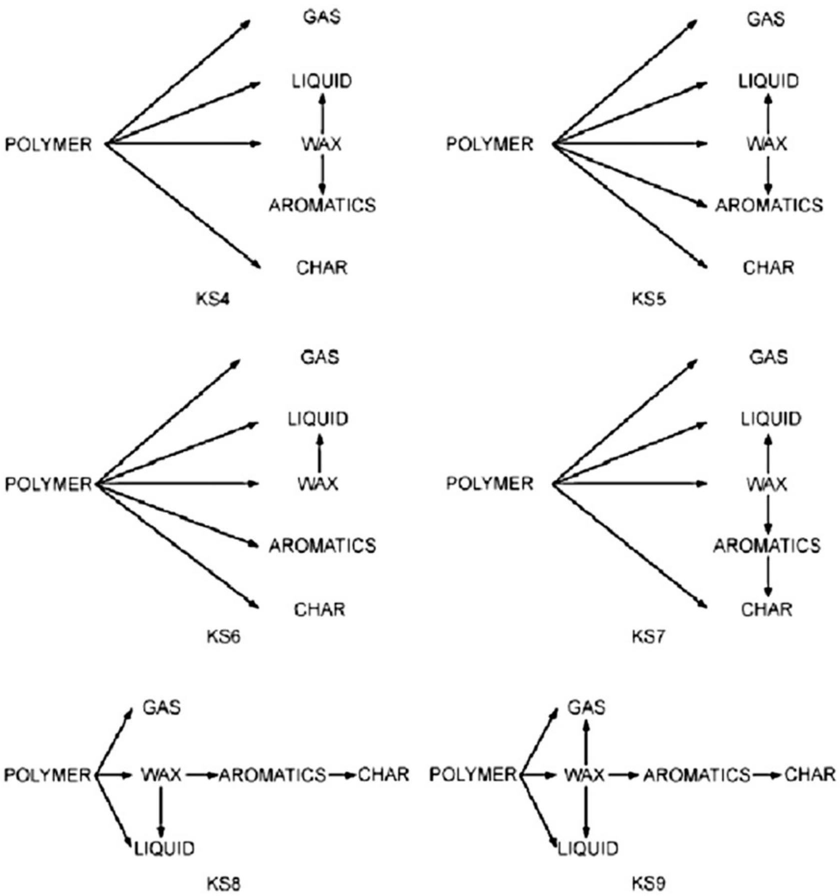

Fig. 1. Suggested simplified reaction schemes from the literature.