Microplastics thermal treatment by polyethylene terephthalate-biomass gasification

Raquel Tavares[a], Ana Ramos[b,c], Abel Rouboa[a,c,d,*]

[a] University of Trás-os-Montes and Alto Douro, Vila Real, Portugal
[b] INEGI-FEUP – Faculty of Engineering of the University of Porto, Porto, Portugal
[c] LAETA-INEGI – Faculty of Engineering, University of Porto, Porto, Portugal
[d] MEAM Department, University of Pennsylvania, PA 19020, Philadelphia, USA

ARTICLE INFO

ABSTRACT

In this paper, a previously developed Aspen Plus model for gasification of biomass was adapted to the gasification of microplastics in a temperature range of 400–1200 °C. The effect of parameters such as equivalence ratio (ER), steam-to-biomass ratio (SBR) and gasification temperature in hydrogen production was evaluated, as well as three different gasifying agents namely air, O_2 and steam were tested. The relationship between all these variables was assessed in order to better characterize the final syngas. Results showed that for higher hydrogen yields, microplastics composition should be majorly polyethylene terephthalate (PET), assuring H_2 molar fraction contents in the order of 63–66%. The achieved lower heating value (LHV) was 9.2 MJ/Nm³ which endorsed high-quality syngas.

1. Introduction

Although society is gradually more aware of alternative energies, fossil fuels are still the most utilized source for the production of electricity [1]. In 2016, approximately 33% of the world primary energy consumption was oil-based while 28% was coal-based, alternative energies being reduced to a lower share, wind providing more than half of the renewable share [2].

One of the sources that has been used to produce alternative energies are plastics, once they are commonly present in our daily routines and their use has been significantly growing due to the actual society demand, municipal solid wastes being composed of a high percentage of plastics [3]. Nowadays, besides the issues regarding the safe disposal of plastics, a novel concern deals with the occurrence of microplastics in the environment, as reported in recent reviews in this matter [4,5]. Microplastics are plastic particles with diameter ≤ 5 mm, with two possible origins: primary, directly entering the environment, mostly as raw material from the plastic industry or as micro-components present in cosmetic or hygiene products like toothpastes, shampoos, soaps or lotions [6]; secondary, indirectly appearing in the environment from the degradation of bigger plastic fractions due to the action of climatic conditions or physical elements, like sunlight or erosion [7]. Independently of their source, microplastics become easily available to the existing wildlife, possibly causing death or harm

[8–11]. Some authors have already characterized fractions of microplastics in sediments assessed in natural reserves revealing their polymer types and also their additive contents [12,13]. Potential scale-up effects which may affect mankind through seafood and fish intake have also been reported [14,15].

So far, common treatments applied to these plastic waste streams included incineration and landfilling (among others), which constitute less interesting options in what regards environmental sustainability, leading to a quest for improved solutions in which marketable products could be attained [16,17]. In regards to these enhanced treatments, several researchers have been studying other handling and thermal processing techniques, aiming to achieve environmental benefits such as the reduction of fossil fuels in power production due to the energy recovery from plastic waste [18,19]. From these, gasification is one of the most promising techniques assuring high efficiency in feedstock conversion and producing an versatile final gas, syngas [20]. The main reactions occurring during gasification is shown in Fig. 1, and the sequence of events briefly consists in: (a) pyrolysis/devolatilization at low temperature, where liquid and gaseous fractions as well as tar are produced from the initial feedstock; (b) decomposition of these products by additional heat supply giving rise to a gaseous mixture of smaller molecules; (c) char gasification, which originates syngas (composed of CO, CO_2, H_2 and light hydrocarbons) [21].

Syngas may have several appliances such as production of

Oxidation reaction

Volatiles

$$CO + 1/2O_2 \leftrightarrow CO_2 \quad \Delta H = -283kJ/mol$$

$$H_2 + 1/2O_2 \leftrightarrow H_2O \quad \Delta H = -242kJ/mol$$

Char

$$C + 1/2O_2 \leftrightarrow CO \quad \Delta H = -111kJ/mol$$

$$C + O_2 \leftrightarrow CO_2 \quad \Delta H = -394kJ/mol$$

Boudouard reaction

$$C + CO_2 \leftrightarrow 2CO \quad \Delta H\ -172kJ/mol$$

Water-Gas reaction

Primary

$$C + H_2O \leftrightarrow CO + H_2 \quad \Delta H = -131kJ/mol$$

Secondary

$$C + 2H_2O \leftrightarrow CO_2 + 2H_2 \quad \Delta H = -90kJ/mol$$

Methanation reaction

$$C + 2H_2 \leftrightarrow CH_4 \quad \Delta H = -75kJ/mol$$

Water-Gas shift reaction

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad \Delta H = -41kJ/mol$$

Steam Reforming reaction

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H = 206kJ/mol$$

$$C_nH + nH_2O \leftrightarrow nCO + \frac{(n+m)}{2}H_2$$

Dry Reforming reaction

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad \Delta H = 247kJ/mol$$

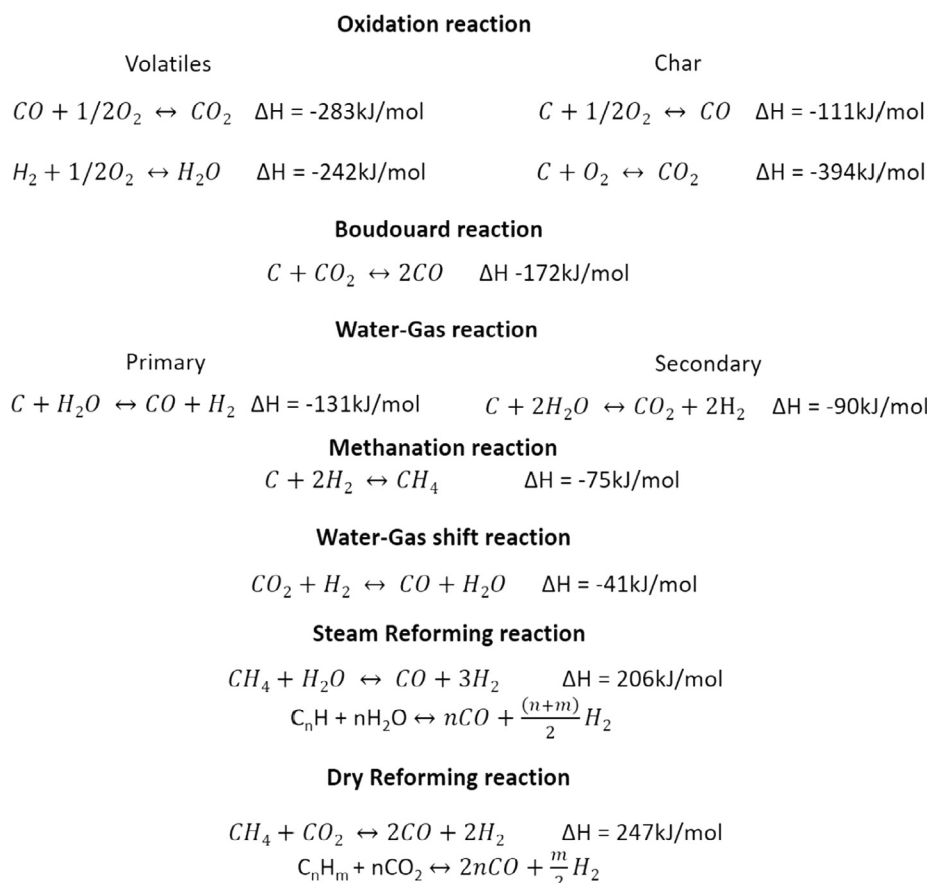$$C_nH_m + nCO_2 \leftrightarrow 2nCO + \frac{m}{2}H_2$$

Fig. 1. Main gasification reactions [21].

electricity through gas turbines or fuel cells, of chemical products that can later be used in industry and even hydrogen generation or alike fuels for transport sector [22,23]. Gasification of plastics has been studied for the last decades as an attempt to substitute current waste processing techniques by more sustainable and environmental-friendly options [24].

Many studies have already reported the gasification of plastics, monitoring the influencing factors as well as the achieved syngas quality depending on the type of plastic used [21], and even suggested this technique as the potentially most favourable to degrade microplastics [25]. Pinto et al. [22] assessed PE and biomass co-gasification, concluding that higher PE ratios enhanced H_2 contents on the final syngas. Kannan et al. [26] also assessed PE debris gasification, analysing the influence of variables like ER, temperature and steam atmosphere. Regarding PET debris gasification, several concluding remarks may be drawn from published works by Robinson et al. [1] and Kannan et al. [27], among others. As a matter of fact, some authors report difficulties such as feeding problems and contaminants formation when gasifying plastics alone, which may be promptly attenuated if biomass is used as co-fuel [1,21,22,28]. Actually, Narobe et al. [29] presented a kinetic study for the co-gasification of biomass and plastics in comparison to the gasification of plastics alone both by developing a numerical model to simulate the experiments and also running them in a pilot plant. Successful thermochemical conversion was verified in the case of co-gasification, the first step of the process (pyrolysis) playing a determinant role in the final outcome. Thermal conduction was described by Lah et al. [30] as the limiting step during pyrolysis, since it constitutes the predominant mechanism of heat transfer in plastic materials' degradation. The aim of this work was to validate a computational model under the Aspen Plus environment, to study low temperature gasification of microplastics. Three gasifying agents (air, oxygen and steam) were evaluated, as well as the influence of adding biomass to the microplastics fraction, in a 50–50% to 90–10% ratio of microplastics-biomass. For each of the varying conditions, ER, temperature, SBR, H_2 content, CGE and LHV were assessed.

2. Numerical model

The minimum energy principle of Gibbs was applied, as described in detail in [31] (please see Supplementary Information Section for detailed equations).

The feedstock was named PET/BIO and was sent to a heat exchanger (DRIER) where moisture was removed and calculated through a localized calculator (WATER CALCULATOR). The first separating module (SEP1) simulated the splitting of the flow coming from the heat exchanger in two new streams: water and dry material (DRY-FEED), this last one being decomposed in a module (DECMPOSE) where pyrolysis of all the components occurred and their yields were calculated (YIELD CALCULATOR). After the decomposition, the gaseous stream was sent to the GASIFIER, where gasification took place. One of the three different gasifying agents (O2, AIR or STEAM) was applied in the gasifier, after which the obtained flow was directed to a new separation module (SEP2), where gas cleaning was held. Fig. 2 shows the developed model.

3. Method

3.1. Fuel

Microplastics were constituted by PETand provided by Yangli Mechanical and Electrical Technlogy Co, Ltd, according to [32]. Biomass was assessed by Favas et al. [33]. Table 1 depicts PET and biomass composition.