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Comparison of steam reforming and partial oxidation of biomass pyrolysis tars over activated carbon derived from waste tire

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ABSTRACT

The main objective of this work was to analyze catalytic tar destruction in order to compare the performance of two thermochemical processes, partial oxidation and steam reforming. Activated carbon, derived from char obtained in fast pyrolysis of waste tires, was used as a catalyst. The efficiency of this catalyst was analyzed with respect to its ability to decompose tar-forming hydrocarbons at high temperatures, and the optimal conditions of the process were determined.

Results of catalytic steam reforming and partial oxidation of real tars from biomass pyrolysis are presented in this article. Tar destruction was performed in a fixed bed reactor at temperatures from 700 °C to 900 °C, with the steam-to-carbon ratio (H_2O/C) from 0 to 1, air equivalence ratio (ER) from 0 to 0.5 at a constant space velocity and the initial concentration of tars $21.1 \pm 1.89\ \mathrm{g/m^3}$. The thermal destruction of tars was found to be most intensive in terms of both tar destruction and hydrogen gas production when using steam reforming at 900 °C and $H_2O/C = 1$. Under these conditions, an almost complete conversion of tars was achieved, with benzene as the only remainder at a concentration of $0.019\ \mathrm{g/m^3}$.

1. Introduction

Tars still remain one of the main challenges in promoting the development of biomass or waste gasification systems. Producer gas cleaning from sticky tars is necessary before applying the gas directly to internal combustion engines, gas turbines or for synthetic gas production. However, tar conversion to gaseous products or hydrocarbons with a lower dew point is advantageous not only in terms of cleaning impurities which tend to deposit on cold equipment parts, but also for retaining the energy efficiency of the process. According to Samsudin and Zainal [1], thermal and catalytic tar removal methods are more attractive than mechanical treatment because of the complete destruction of tars and preservation of energy conversion efficiency. Certainly, part of energy will be consumed to maintain the reaction temperature at an appropriate level. Many works published elsewhere give considerable attention to developing an efficient gasification process for the production of clean gas free of tars and particulates. They also examine conversion of tars by employing thermochemical catalysis, new catalysts, and converters. Conclusively good review articles [1–4] suggest the carbonaceous residue, char or charcoal obtained in the pyrolysis of organic matters as one of the cheapest catalysts to convert tars. The efficiency of tar destruction in the presence of char is similar to that of naturally available catalysts, such as dolomite, as stated by Striugas et al. [5]. Thermal cracking, partial oxidation and steam reforming are the main processes for the thermal conversion of tars in the presence of char.

Gilbert et al. [6] investigated catalytic tar cracking using char as a catalyst. Experiments were performed at reaction temperatures between 500 and 800 °C. Thermal cracking was responsible mainly for tar destruction at higher temperatures. A longer vapor residence time is required in order to fully crack tars. Steam as a gasifying agent, either with or without oxygen, is recommended. The effect of temperature and residence time on tar cracking over the biomass char was also investigated by Dutch authors [7]. Tar reduction is evident, but a longer hot zone contact time was needed. Chen et al. [8] have analyzed tar cracking at various temperatures and residence times with different char particle sizes and char types in a two-stage reactor. They concluded that tar destruction becomes more intensive with increasing the reaction temperature, residence time and decreasing of char particle size. Tar cracking using activated carbon in a lab-scale two-stage gasifier was performed by Mun et al. [9,10]. Carbon activated at a temperature of 793 °C showed a significant effect on the conversion of tar compounds to lighter hydrocarbons and H_2 yield. Dabai et al. [11] examined tar cracking in a two-stage fixed bed reactor. The achieved results showed that the char bed enhances the destruction of tars by up to 99.1% at a temperature of 1000 °C. Moreover, the char-catalyzed cracking of biomass tars

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in a two-stage fixed bed reactor was investigated by Sun et al. [12]. The catalytic effect of char was noticeable at a lower temperature range (500–600 °C). With increasing the temperature, the catalytic effect of char vanished because of the intensified thermal effect.

It is evident from the review of the above-mentioned literature that char has a catalytic effect on tar cracking. However, to achieve a full conversion, a gasifying agent should be introduced. Steam reforming of tar derived from biomass pyrolysis over char and char-supported catalyst was investigated by Min et al. [13]. The introduced steam showed only a negligible influence on tar destruction at higher temperatures, if compared with the reforming and pyrolysis without a catalyst. Hosokai et al. [14] explored the decomposition of two tar compounds, benzene and naphthalene, over charcoal at a temperature of 800–900 °C and in a steam atmosphere. The conversion ratio of naphthalene was over 99.99% at every tested temperature and gas residence time of 0.2 s. At the same conditions the conversion of benzene was lower, i.e. 84–98%. Also, Abu El-Rub [15] performed an experimental comparison of biomass chars with other catalysts for steam reforming of tars. The conversion of real tars in a char bed at a temperature of 850 °C was about 97%. The mean concentration of tars in the producer gas remained 115 mg/Nm^3. Only benzo(a)pyrene and naphthalene were found in the outlet gas at a temperature of 800 °C and 750 °C, respectively.

Chen et al. [8] compared tar cracking with partial oxidation over a second-stage char bed in the temperature range of 900–1000 °C. The experimental investigations showed the effect of air: the introduction of air without a catalyst resulted in a reduction of tar concentration in the producer gas; after introducing char with air, a further reduction of tar was achieved. A two-stage pilot scale biomass gasification reactor with tar reduction was developed, and its suitability for tar reduction and power generation was reported in Ref. [16]. Partial oxidation of tars over a char bed in the second stage reactor was evident; the producer gas contained only 45 mg/m^3 of tar remainder. The only negative aspect of this process was a high air equivalence ratio (up to 71%) which impacts energy conversion efficiency.

The effect of char introduced in the destruction of tar was quite noticeable. Moreover, the effect of steam or air reforming, compared with tar cracking, was also obvious. A comparison of partial oxidation and steam reforming for non-catalytic destruction of tar was presented in the work of Wang et al. [17]. They examined the changing air equivalence ratio, steam-to-carbon ratio and residence time, the destruction of tars derived from biomass and polyethylene pyrolysis at a constant temperature of 900 °C. A comparison of the results presented in the article shows that the supply of air (oxygen) into the reformer was more effective than the supply of steam for reducing the tar residual rate. However, it is still unclear which process – partial oxidation or steam reforming – is preferred for tar reforming over char or an activated carbon bed.

For some time, the charcoal obtained from biomass pyrolysis has mostly been used elsewhere. A research group at the Lithuanian Energy Institute (LEI) has developed a reactor for a fast gasification of used tires, where char is produced as a by-product. The residual char may be used for direct combustion as a fuel or for the proposed thermal catalytic tar cracking. Thus, this study presents a comparison of the partial catalytic oxidation and steam reforming of real tars over activated carbon. Activated carbon is produced from char obtained from the pyrolysis of waste tires. The efficiency of tar conversion at various reaction temperatures, air equivalence ratios and steam-to-carbon ratio was evaluated. The obtained results are applicable to all types of gasifiers that produce tars.

Table 1
Properties of activated carbon used in the experimental investigation.

Particle size (mm)	2.2–1.1
Bulk density (g/cm^3)	0.187
BET surface area (m^2/g)	363
Langmuir surface area (m^2/g)	477
Total pore volume (mm^3/g)	261
Micropore volume (mm^3/g)	106
Micropore area (m^2/g)	302
Mean pore diameter (nm)	8.92

2. Materials and methods

2.1. Preparation of catalyst

Scrap tires were gasified in a muffle furnace at 850 °C. After about 10 min all volatile materials were released from tires, and porous char structures were formed. The remaining steel cords were removed from the char; then the char was milled and sieved to a particle size of 2.2–1.1 mm. The obtained char fraction was placed into a heating chamber for activation under a steam atmosphere at a temperature of 850 °C for 2 h. The properties of activated carbon after the activation process are presented in Table 1.

2.2. Experimental setup and procedure

Fig. 1 presents the schematic diagram of experimental setup which consists of three main parts: the biomass pyrolysis reactor, the catalytic fixed bed reactor, and the sample preparation system. A more detailed explanation of the experimental procedure was described elsewhere [5]. In this paper, only relevant modifications and the main working parameters will be discussed.

Commercially available wood pellets made from softwood, mainly spruce and pine (JSC Baltwood), were used for the production of a tar-rich gaseous mixture in the pyrolysis reactor. The properties of wood pellets used in the experiments are presented in Table 2. The ultimate and proximate analysis was performed using an IKA C5000 calorimeter and a Flash 2000 analyzer by standard methods (EN 14918:2009, CEN/TS 15104:2005, EN 14775:2009 and EN 14774-1:2009).

At a temperature of the pyrolysis reaction set at 850 °C, the composition of the gaseous mixture was determined (Table 3). In each run of the experiments, the fuel feeding rate was kept constant at 5 g/min. The initial concentration of calibrated tars in the producer gas was 21.1 ± 1.89 g/m^3. Nitrogen was used in all experiments as a carrier. The resulting gas mixture entered the tar conversion reactor with an activated carbon bed. Differently from the previous work [5], the catalytic bed had a constant catalyst volume (470 ml). This volume was identified as optimal for the full destruction of tars with the initial concentration of 21.1 g/m^3. In order to compare tar destruction efficiency using partial oxidation and steam reforming over an activated carbon bed, several experiments were performed. First of all, the optimum air equivalence (ER) and steam-to-carbon (H_2O/C) ratios at a constant temperature were determined. Then,

Table 2
Properties of wood pellets.

Ultimate analysis (% dry basis)	
C	49.20
H	6.20
O (diff.)	44.46
N	0.08
S	0.06
Proximate analysis (% total)	
Ash	0.35
Moisture	5.2
Lower heating value (MJ/kg)	19