



Upgrading producer gas quality from rubber wood gasification in a radio frequency tar thermocatalytic treatment reactor



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HIGHLIGHTS

- The use of radio frequency energy to produce high quality producer gas was studied.
- Gas heating value improved as the thermocatalytic temperature increases.
- The cleanest producer gas was obtained with dolomite.
- Feasible producer gas for internal engine application was obtained.

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ABSTRACT

This study focused on improving the producer gas quality using radio frequency (RF) tar thermocatalytic treatment reactor. The producer gas containing tar, particles and water was directly passed at a particular flow rate into the RF reactor at various temperatures for catalytic and thermal treatments. Thermal treatment generates higher heating value of 5.76 MJ Nm⁻³ at 1200 °C. Catalytic treatments using both dolomite and Y-zeolite provide high tar and particles conversion efficiencies of about 97% on average. The result also showed that light poly-aromatic hydrocarbons especially naphthalene and aromatic compounds particularly benzene and toluene were still found even at higher reaction temperatures. Low energy intensive RF tar thermocatalytic treatment was found to be effective for upgrading the producer gas quality to meet the end user requirements and increasing its energy content.

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1. Introduction

Biomass gasification is an efficient and environmentally friendly method to produce gaseous fuel (producer gas) for heat and power generation through internal combustion engine, gas turbine and fuel cell as well as for chemical synthesis applications such as methanol, methane and Fischer–Tropsch liquids. However, producer gas is always accompanied by undesirable products such as tar and particulates. Until now, tar presents as the main obstacle in biomass gasification for not only causing serious operational problems in downstream pipeline and end user application but also affecting the energy efficiency of the overall process. Therefore, removal or conversion of tar as well as particulates from producer gas is indispensable.

Since three decades ago, various producer gas cleaning methods have been developed and reported in numerous literatures with the aim to produce high quality producer gas for end user

application. In general, these methods are classified into two categories, namely: primary methods that consist of gasifier design and optimization of operating conditions and secondary methods that consist of mechanical and thermocatalytic treatments (Anis and Zainal, 2011; Devi et al., 2003). From technical point of view, a combination of the two methods guarantees a more satisfactory quality of producer gas (Gil et al., 1999). Moreover, appropriate implementation of thermocatalytic treatment is more favorable due to converting tar into useful gases such as hydrogen, carbon monoxide or hydrocarbon gases which can improve the producer gas energy content.

Until now, it is undeniable that thermal treatment process improves the composition of the producer gas, however little attention has been paid in its development since it requires high additional energy to achieve the desired operating temperatures. Literatures show that most of the heavy tar can be cracked at a temperature of 900 °C (Qin et al., 2007). Even so, to achieve sufficiently high tar conversion efficiency, temperatures of more than 1100 °C are needed (Jess, 1996; Zhang et al., 2010). In another approach, catalytic treatment processes have gained more

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attention. In particular, there have been ongoing efforts for developing more economical catalysts for tar conversion. For this reason, the utilization of natural catalysts such as dolomite and zeolite or their impregnation on metal catalysts would be a wise choice.

The activity of calcined dolomite was found to have better tar conversion activity in biomass gasification (Delgado et al., 1997). Its activity also depends on where the natural dolomite is obtained (Gusta et al., 2009; Yu et al., 2009). The use of zeolites for biomass tar conversion has also been reported but is still rare. In most of the published literatures biomass tar model compounds were used instead of real tar from producer gas such as benzene, toluene, naphthalene, and 1-methylnaphthalene (Anis et al., 2013; Buchireddy et al., 2010; Dou et al., 2003; Radwan et al., 2000). Recently, the application of natural calcined zeolites to remove the tar from biomass gasification has been observed (Chiang et al., 2012, 2013; Mun et al., 2013).

Although various efforts of producer gas cleaning methods have been performed and proven technically effective as described above but from an economic point of view, efficient removal of tar still remains the major technical obstacle to the success in commercialization of biomass gasification technologies on a large scale. In general, overall process of existing thermocatalytic treatments of tar is costly due to the use of conventional heating mechanism that consumes high electrical energy. Related to the heating process of a substance within the reactor, conventional heating transfers heat from the surface into the interior of the reactor by conduction, convection and/or radiation, principally known as surface heating. This is often a slow process, requiring high external temperatures and thus more energy against heat transfer resistances and heat losses to surrounding to generate the temperature differences required inside the reactor (Salema and Ani, 2011). Thereby, radial temperature distribution is also non-uniform where the surface is much hotter than the inside of the reactor. In several reaction processes, this phenomenon is commonly known as wall effect.

Based on the preceding concerns, implementation of radio frequency (RF) energy for thermocatalytic treatment of tar would be a more realistic option. In this method which commonly utilizes microwave, the transfer of energy into the material occurs instantaneously through molecular interaction with the electromagnetic field (Thostenson and Chou, 1999). The unique feature of volumetric heating of this technique can result more rapid heating process of the reactor in the presence of susceptor material (Anis et al., 2013) resulting in significant energy saving, reduce process time, increase process yield and environmental compatibility (Yin, 2012). For this reason, a simple and rapid test technique has been developed by using RF energy which is not only effective but has also low energy consumption. The performances of this technique has been demonstrated and reported in our previous paper for thermocatalytic treatment of tar using toluene and naphthalene as tar model compounds (Anis et al., 2013).

This work was conducted to examine the capability of RF thermocatalytic treatment reactor in improving the quality and production of producer gas. The producer gas containing tar and particulates was continuously produced from rubber woodblocks gasification in a suction fixed bed downdraft gasifier. The effects of temperatures and catalysts (calcined dolomite and Y-zeolite) on the yield of products including tar, particles, and gas composition as well as high heating value (HHV) of producer gas were studied.

2. Methods

2.1. Materials

In this study, rubber wood leftovers from furniture industries were used as biomass material for the production of producer gas

in a suction throatless downdraft fixed bed gasifier. The feed material was prepared into small pieces with a size of approximately 2–3 cm cube. Proximate analysis showed that the feed material was comprised of 11.4 wt.% of fixed carbon, 78.3 wt.% of volatile matter, 0.2 wt.% of ash and 10.29 wt.% of moisture. Whilst elemental analysis revealed that it was composed of 44.80 wt.% of carbon, 12.19 wt.% of hydrogen, 0.45 wt.% of nitrogen, 0.88 wt.% of sulfur and 41.68 wt.% of oxygen. The HHV of the feed material determined using an automatic bomb calorimeter was 20.6 MJ kg⁻¹.

Dolomite and Y-zeolite were used to investigate the influence of catalysts on tar cracking. The catalysts were calcined in situ under air flow for 2 h at 900 °C for dolomite and 600 °C for Y-zeolite. Dolomite has a particle size of 600 μm with a bulk density of 1.33 g cm⁻³. It was mainly composed of 34.69 wt.% CaO, 15.06 wt.% MgO and 2.34 wt.% SiO₂. Y-zeolite is a commercially powder catalyst (CBV720) with a bulk density of 0.26 g cm⁻³ and SiO₂/Al₂O₃ of 30. Other properties of both catalysts are given in supplementary material (Table SM-1).

2.2. Experimental apparatus

The schematic of overall experimental setup is given in supplementary material (Fig. SM-1). It consists of three main units: gasifier, producer gas treatment and gasification product collection systems. The system includes a suction throatless downdraft fixed bed gasifier, cyclone separator, condenser, blower, and a flare port. The gasifier with an inner diameter of 0.15 m and height of 1.05 m has a thermal power output of 10 kW_T corresponding to 6 kg h⁻¹ biomass feeding rate. An orifice meter with a differential pressure transducer was used to measure the pressure drop for flow rate quantification of the producer gas.

Producer gas treatment system includes a modified RF oven and a reactor containing silicon carbide (SiC) as susceptor material. The modified RF oven (Panasonic, NN-SM330 M) has a frequency of 2.45 GHz corresponding to wavelength of 12.23 cm. The maximum power consumption and maximum output power of the RF oven were 1125 and 700 W, respectively. The alumina reactor (25.4 mm i.d. and 160 mm length) was installed vertically in the RF chamber and designed as a fixed bed reactor. To absorb and convert RF energy into heat, SiC with a particle size of 2.085 mm and bulk density of 1.48 g cm⁻³ was employed. This system is also called RF tar treatment system and has been fully described in a previous study (Anis et al., 2013). For maintaining the temperature inside the reactor, a temperature controller was also attached to the system.

Gasification product collection system consists of a tar sampling train, flow meter, vacuum pump and a gas sampling bag. The tar sampling train has been modified along with the guideline for sampling and analysis of tar and particles in producer gas (Paasen et al., 2002). The producer gas passes through a series of six impinger bottles. The first two bottles were placed at atmospheric environment and the second four bottles were immersed in a mixture of ice and salt bath with temperature of about -22 °C. In addition, the first five bottles were filled with 50 mL isopropanol whilst the last was empty. The consideration of the modified tar sampling train is based on the behavior of tar produced by downdraft gasifier that is mainly composed of class 3 and 4 tar (Milne et al., 1998). Vacuum pump was used to extract the producer gas into the RF tar treatment system. A flow meter measures the flow rate of dry clean producer gas through the RF reactor and gasification product collection system.

2.3. Experimental procedure

2.3.1. Thermocatalytic treatment

For each experiment, a portion of the raw producer gas generated from rubber wood blocks gasification was taken after the condenser (see Fig. SM-1 in supplementary material) and then

extracted into the RF tar treatment fixed bed reactor at a particular flow rate to give the desired residence time. The rest of the raw producer gas was burned on the flare port. In thermal treatment, the temperature was varied from 900 to 1200 °C whereas the residence time was in the range of 0.12–0.13 s. In catalytic treatment, the catalyst with SiC bed is sandwiched between SiC beds, forming a total bed height of 120 mm within the reactor. In each experimental run, 6 g of dolomite or 3 g of Y-zeolite was mixed with 25 g of SiC. The residence time within the catalytic bed at the reference temperature was in the range of 0.12–0.18 s. The catalytic bed temperature for dolomite was conducted at temperature of 700–900 °C in order to minimize the thermal treatment effect whilst for Y-zeolite the temperature was 500–700 °C due to catalyst thermal stability (Gates, 1992).

2.3.2. Sampling and analysis of the product

Before and after leaving the RF tar treatment reactor, the gas stream was passed into a tar sampling train containing organic solvent of isopropanol to condense and absorb the tar as well as particulates. Once the samples have been collected, they were mixed together and filtered to separate the particles through preweighed qualitative filter paper (Whatman, 90 mm diameter) into a flask. The filter paper containing particles was dried in an oven and then weighed to obtain final weight. The difference of initial and final weight of the filter paper was considered as yield of particles. The filtered solvent was evaporated by a standard rotary evaporator equipped with solvent library software. Gravimetric tar yield was obtained by the weight of the dry residue normalized by the collected gas volume. Tar samples were analyzed using gas chromatography–mass spectrometry (GC–MS) analyzer combined with NIST MS 2.0 software. The dry clean gas product was collected using a gas sampling bag and then analyzed in a gas chromatography–thermal conductivity detector (GC–TCD) to quantify producer gas composition using He as a carrier gas. Three samples were taken to obtain the average.

2.3.3. Calculation of equivalence ratio and gas heating value

In this work, the biomass gasification was run under a fixed condition for each experimental study. In order to reduce the number of parameters affecting the performance of the biomass gasifier, an equivalence ratio (ER) of 0.26 was maintained constant. ER reflects the combined effect of airflow rate, rate of wood supply and duration of the run that can be calculated based on the following equation (Zainal and Rifau, 2002):

$$ER = \frac{\text{Air flow rate}}{\text{Biomass consumption rate}} \bigg/ \frac{\text{Air flow rate}}{\text{Biomass consumption rate}} \bigg|_{\text{Stoichiometric}} \quad (1)$$

The stoichiometric ratio of air flow rate to biomass consumption rate is 5.22 m³ air/kg of wood (Zainal and Rifau, 2002).

Evaluations of the gasification performance such as gas yield, carbon conversion efficiency and cold gas efficiency were excluded because only a fraction of the producer gas can be processed in the RF reactor. Thus, in this study the producer gas quality was characterized by the tar and particles contents, producer gas compositions and high heating values (HHV) of the producer gas. HHV (MJ Nm⁻³) of the producer gas is dependent on the percentage volume fraction (X) of H₂, CO and CH₄ and can be calculated by the following equation (Waldheim and Nilsson, 2001):

$$HHV = 12.766X_{H_2} + 12.6441X_{CO} + 39.847X_{CH_4} \quad (2)$$

3. Results and discussion

Since the raw producer gas is taken after the condenser and directly introduced into the RF reactor without gas pre-filter, it

contains not only producer gas (H₂, O₂, N₂, CO, CH₄ and CO₂) and tar but also particulates and water. The result showed that the raw producer gas was typically consisted of 94.25 wt.% of gases, 0.19 wt.% of tar, 0.04 wt.% of particles and 5.51 wt.% of water. Meanwhile, the producer gas was mainly composed of 12.96 vol.% of H₂, 16.67 vol.% of CO, 1.77 vol.% of CH₄, 12.89 vol.% of CO₂, 3.16 vol.% of O₂ and 52.55 vol.% of N₂. Consequently, several reactions take place simultaneously during thermocatalytic treatment of producer gas tar in the RF reactor.

3.1. Thermal treatment of tar

Gas compositions and HHV of producer gas from thermal treatment process at various temperatures are shown in Fig. 1. H₂ content seems to decrease from the initial condition after thermal treatment at 900 °C. Hydrocracking of tar and hydrogasification of solid particles take more prominent role at this condition that consume more H₂, resulting in increasing CH₄ production. The increase of CO formation is mainly formed by partial oxidation of solid particles. Fig. 2 displays the yields of tar and particle as a function of temperature. More than 85% of the particles were consumed and converted into gases whilst tar conversion reached only about 50% at 900 °C showing less contribution of tar cracking and reforming reactions for H₂ production. Compared to other similar studies, this system resulted in lower tar conversion efficiency due to the presence of light aromatic and light poly-aromatic hydrocarbon which are relatively stable.

The gas composition shows different behavior at higher temperatures where the formation of combustible gases become more intense. Thermodynamically, when the reaction temperature increases, CO and H₂ formation increases whilst CO₂ and CH₄ formation decreases. The presences of O₂, H₂O and particles support the production of combustible gases by means of water gas reaction, Boudouard reaction, and partial oxidation. According to Le Chatelier's principle, the high reaction temperatures favor the first two endothermic reactions. Moreover, the conditions also occur due to the high activity of tar cracking and reforming reactions. In the meantime, CH₄ content shows slight improvement from 900 to 1000 °C and then decreases as the reaction temperature increases. The reduction of CH₄ content at higher temperature is mainly caused by steam and dry methane reforming reactions. These reactions are also endothermic, meaning the forward reaction is preferred at higher temperatures. As a result, the gas heating value is enhanced by about 18% at the highest reaction temperature of 1200 °C. More than 90% and 98% tar and particle conversion efficiencies were obtained, respectively. These results correspond to the tar and particle concentration of 147 and 4 mg Nm⁻³, respectively. This achievement is in line with other studies where complete conversion of tar and particle in the producer gas requires extremely high temperatures above 1200 °C (Zhang et al., 2010).

Tar compounds identified by GC–MS from raw producer gas and after thermal treatment processes of producer gas tar are shown in Table 1. Tar species contained in raw producer gas generated by downdraft gasification of rubber woodblocks include heterocyclic compounds (e.g., phenol and benzofuran), aromatic compounds (e.g., benzene, toluene, xylene, ethylbenzene, styrene, indene and methylindene), light poly-aromatic hydrocarbons (PAHs) (e.g., naphthalene, methylnaphthalene, fluorene and anthracene) and heavy PAHs (e.g., pyrene, fluoranthene, chrysene and acepyrene). It can be note that these compounds are commonly identified in the case of biomass downdraft gasification (Milne et al., 1998; Paasen et al., 2002). The identified tar compounds changed considerably when the producer gas tar was allowed to pass within the high temperature of RF reactor. Some of tar species especially aromatic compounds (e.g. xylene, ethylbenzene and styrene), light

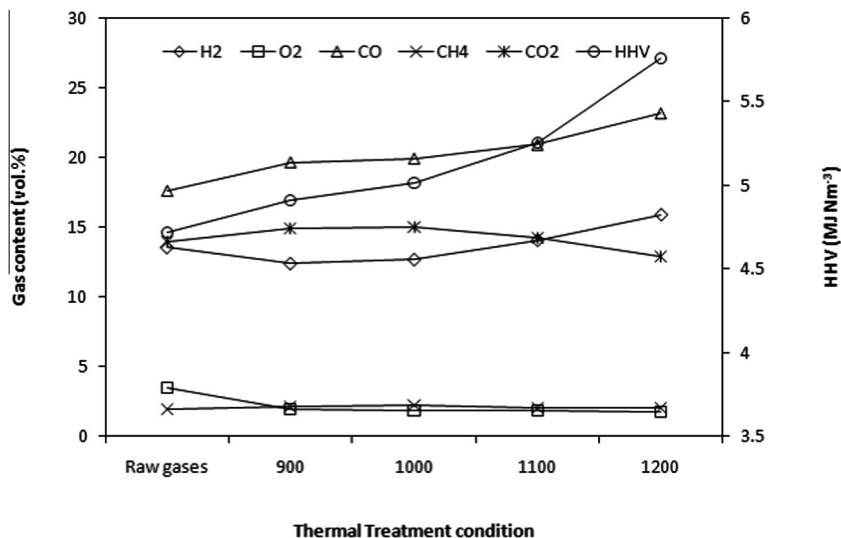


Fig. 1. Gas composition and HHV during thermal treatment of producer gas.

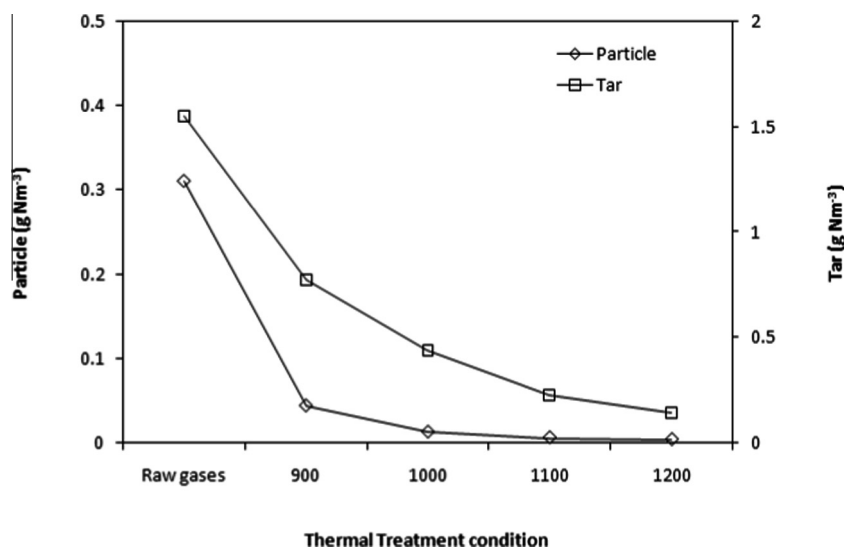


Fig. 2. Tar and particle concentration during thermal treatment of producer gas.

PAHs (e.g. methylnaphthalene, fluorene and phenanthrene) and heavy PAHs (e.g. benzo[b]fluorine, chrysene and acepyrene) were not detected during thermal treatment at 900 °C. Increasing the reaction temperature up to 1200 °C, it can be seen that only benzene, toluene, indene, naphthalene, biphenyl and anthracene can be found in tar species. In addition more than 70% of tar species was occupied by benzene and naphthalene. This result confirms the high stability of these compounds during thermal treatment process (Anis et al., 2013; Zeng et al., 2011; Zhang et al., 2010).

3.2. Catalytic treatment of tar

3.2.1. Dolomite

The activities of dolomite on catalytic treatment of producer gas tar were studied at temperatures from 700 to 900 °C. The gas residence times within the catalytic bed were 0.12–0.14 s based on the equivalent isothermal bed volume. The yield of producer gas composition and heating value are given in Fig. 3 whilst Fig. 4 illustrates dependency on catalytic reaction temperature of the yield on tar and particle. H₂ and CO contents tend to decrease with a corresponding increase in CH₄ and CO₂ from the initial values at the

catalytic reaction temperature of 700 °C. Interpreting the experimental data, it should be noted that the gas phase reactions may exclusively govern the formation of gases through partial oxidation and methanation reactions. Those reactions consume more H₂ and CO to form CH₄ and CO₂ as the final gas products. Carbon gasification reactions also seem to play an important role in increasing CO₂ and CH₄ content which can be observed from the high particle concentration reduction of about 84% at temperatures of 700 °C as indicated in Fig. 4. Meanwhile, although tar conversion is relatively high, tar cracking and reforming reactions did not significantly contribute to the formation of useful gases. The tar is mainly trapped and converted to coke on the catalyst surface. It was found that the tar conversion efficiency of 65% at 700 °C corresponds to the reduction of tar concentration from 1776 mg Nm⁻³ initially to 619 mg Nm⁻³.

Fig. 3 also shows that as the reaction temperature increases from 750 to 900 °C, CO and CH₄ content increase almost linearly with a decrease in CO₂ content whereas the yield of H₂ does not show significant changes. The increase of CO formation is attributed to the Boudouard reaction which is thermodynamically favorable at higher temperatures. On the other hand, the increase of CH₄

Table 1
Relative area percentage of major tar compounds resulting from thermal treatment of producer gas tar.

Compound name	Molecular weight	Boiling point (°C)	Raw gases	Thermal reaction temperature (°C)			
				900	1000	1100	1200
Benzene	78	80	11.01	23.97	25.06	31.64	35.52
Toluene	92	110.6	13.10	11.62	15.20	14.18	4.40
Styrene	104	145	0.40	–	–	–	–
Ethylbenzene	106	145	0.65	–	–	–	–
p-Xylene	106	138.3	1.26	–	–	–	–
o-Xylene	106	144.5	0.72	–	–	–	–
Benzene, 1,2,3-trimethyl	120	98	0.27	8.81	6.68	–	–
Benzene, (1-methylethyl)-	120	172.8	2.65	–	–	–	–
Benzene, 1-ethenyl-2-methyl-	118	172.8	1.47	–	–	–	–
Benzene, 1-ethenyl-3-methyl-	118	172.8	3.31	9.53	6.03	–	–
Benzofuran	118	174	0.26	–	–	–	–
Phenol	94	181.8	4.82	2.02	–	–	–
Indene	116	182	6.31	3.76	7.16	7.77	10.23
Methylindene	130	199	3.88	7.16	–	–	–
Naphthalene	128	217.9	4.46	13.80	23.98	35.64	34.80
2-Methylnaphthalene	142	241.1	2.19	4.57	4.33	–	–
1-Methylnaphthalene	142	244.7	2.47	3.43	4.41	–	–
4-Butyl-1,1'-biphenyl	210	318	1.46	3.74	4.03	6.23	8.48
Anthracene	178	339.9	1.32	3.14	3.10	4.54	6.57
Diphenylethyne	178	256.1	2.13	–	–	–	–
9H-fluorene-9-methylene-	178	295	0.39	–	–	–	–
Phenanthrene	178	340	0.49	–	–	–	–
Methylenephenanthrene	190	353	2.54	–	–	–	–
Anthracene, 9-methyl-	192	196	1.00	–	–	–	–
4-Methylenephenanthrene	192	197	0.66	–	–	–	–
Fluoranthene	202	384	2.68	2.01	–	–	–
Pyrene	202	404	11.07	2.45	–	–	–
Pyrene, 4,5-dihydro-	204	404	2.92	–	–	–	–
11H-benzo[b]fluorene	216	405	3.81	–	–	–	–
Pyrene, 1-methyl-	216	405	3.50	–	–	–	–
Chrysene	228	448	1.15	–	–	–	–
Acepyrene	226	448	5.31	–	–	–	–

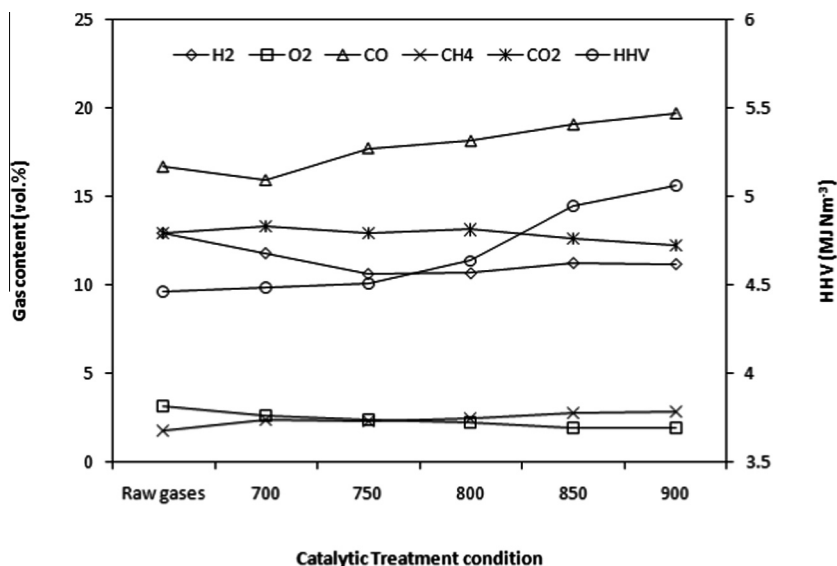


Fig. 3. Gas composition and HHV during catalytic treatment of producer gas using dolomite.

content could be due to the presence of reforming products (H₂, CO, CO₂) that inhibited the occurrence of steam methane reforming reactions on dolomite (Saroglan, 2012). Above 800 °C, the activity of dolomite on catalytic cracking and reforming of tar becomes important and contributes to the formation of valuable gases, which corresponds to the results of another study (Corella et al., 2008). As shown in Fig. 4, the lowest tar and particles content was observed at temperature of 900 °C, in which about 97% tar and 98% particle conversion efficiencies were obtained. These re-

sults correspond to the tar concentration of about 47 mg Nm⁻³ and particle concentration of 6 mg Nm⁻³. The iron content of dolomite is believed to be one of the key factors in improving tar conversion (Gusta et al., 2009). In addition, the relatively higher pore size of dolomite also allows reaction of tar on the surface. This leads to the improvement of producer gas quality, where the gas heating value increased by 12% at a temperature of 900 °C.

Table 2 displays tar components detected during catalytic treatment using dolomite. It has been observed that almost all the tar

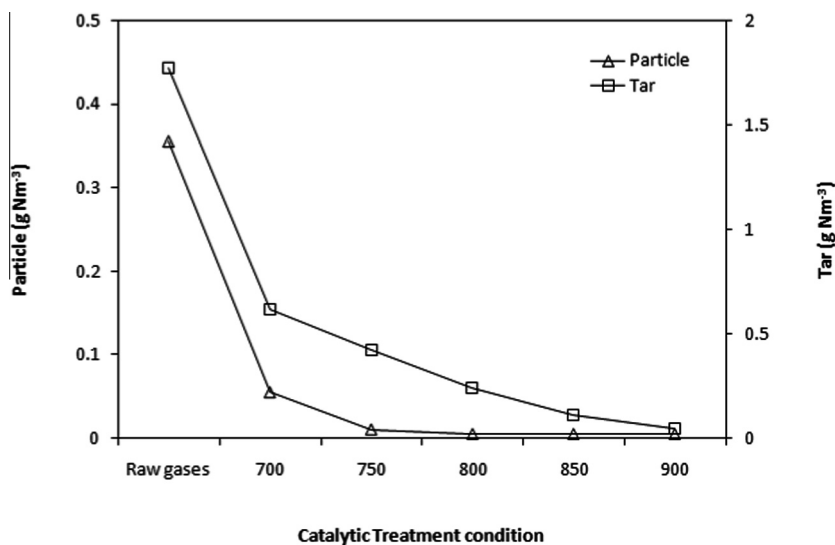


Fig. 4. Tar and particle concentration during catalytic treatment of producer gas using dolomite.

compounds from raw producer gas was found in a lesser amount after catalytic treatment using dolomite at 700 °C. However, it was reduced significantly at higher temperatures particularly above 800 °C. Heterocyclic compounds were not identified at 800 °C due to catalytic cracking activity whilst heavy PAHs especially fluoranthene and pyrene still exist up to 850 °C. An increase in the catalytic reaction temperature to 900 °C, the catalytic activities of dolomite on tar cracking and reforming increased significantly. At this condition, only benzene, toluene, (o-, p-) xylene, naphthalene and anthracene were identified. Among them, benzene was found as the major compound and contributes to more than 45% in tar. Although benzene basically is not considered as a tar, it is formed during the decomposition reactions and its amount increases up to a maximum value with increasing temperature (Devi et al., 2005).

3.2.2. Y-Zeolite

The activities of Y-zeolite as a catalyst on catalytic treatment of producer gas tar at various tested temperatures are shown in Figs. 5

and 6. The experiment was studied at temperatures from 500 to 700 °C and gas residence times of 0.14–0.18 s. The consideration of using relatively low temperature experiments is based on previous studies where Y-zeolite gives better activity on tar model compounds removal at these temperature ranges (Anis et al., 2013; Dou et al., 2003) whereas temperatures over 700 °C can affect thermal stability of Y-zeolite (Gates, 1992). The results in Fig. 5 demonstrate that at catalytic reaction temperature of 500 °C, the yield of CO content remained relatively stable whereas CH₄ increases with decrease of H₂ and CO₂ contents from their initial values. The increase of CH₄ content is thought to be caused by the hydrocracking of tar and hydrogasification of particle. Although tar cracking reactions also occur and produce H₂, but both hydrocracking of tar and hydrogasification of particle consume more H₂, thus lowering H₂ content in the producer gas. The high activities of Y-zeolite on tar and particle conversions can be observed in Fig. 6 where the tar concentration reduced from 1776 to 638 mg Nm⁻³ and the concentration of particle reduced from 355 to 72 mg Nm⁻³ at temperature of 500 °C.

Table 2

Relative area percentage of major tar compounds resulting from dolomite catalytic treatment of producer gas tar.

Compound name	Molecular weight	Boiling point (°C)	Dolomite catalytic reaction temperature (°C)				
			700	750	800	850	900
Benzene	78	80	7.95	14.50	20.74	20.67	45.83
Toluene	92	110.6	15.56	19.71	35.88	38.92	14.60
Styrene	104	145	12.56	–	–	–	–
Ethylbenzene	106	145	7.60	1.85	3.08	5.00	–
p-Xylene	106	138.3	16.26	10.98	6.31	9.51	8.15
o-Xylene	106	144.5	11.42	11.08	18.19	16.91	10.40
Phenol	94	181.8	0.10	0.03	–	–	–
Indene	116	182	0.05	–	–	–	–
Methylindene	130	199	0.12	0.02	–	–	–
Naphthalene	128	217.9	2.95	4.29	5.90	3.58	10.98
2-Methylnaphthalene	142	241.1	0.47	0.79	0.66	0.97	–
1-Methylnaphthalene	142	244.7	0.81	0.84	1.46	–	–
4-Butyl-1,1'-biphenyl	210	318	2.75	4.76	2.15	–	–
Anthracene	178	339.9	1.76	1.44	2.00	3.19	10.02
Phenanthrene	178	340	0.17	–	–	–	–
Methylenephenanthrene	190	353	0.55	0.37	0.58	–	–
Fluoranthene	202	384	0.84	1.98	1.30	0.55	–
Pyrene	202	404	1.39	10.14	1.26	0.71	–
11H-benzo[b]fluorene	216	405	2.15	–	–	–	–
Pyrene, 1-methyl-	216	405	3.05	2.11	–	–	–
Chrysene	228	448	8.97	13.03	–	–	–
Acepyrene	226	448	2.53	2.06	0.48	–	–

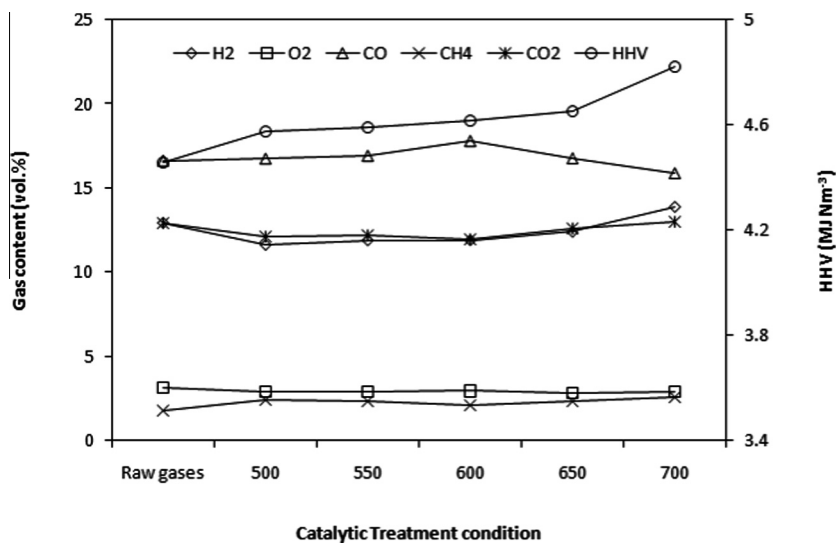


Fig. 5. Gas composition and HHV during catalytic treatment of producer gas using Y-Zeolite.

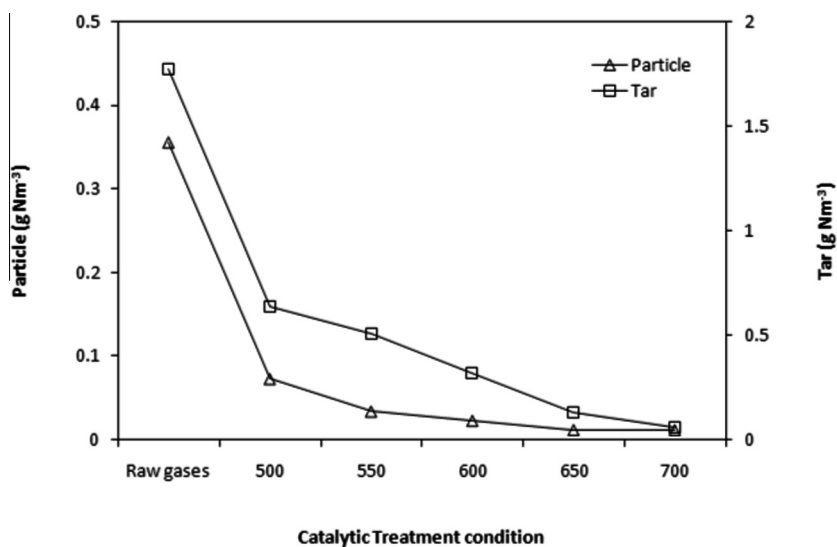


Fig. 6. Tar and particle concentration during catalytic treatment of producer gas using Y-Zeolite.

Table 3

Relative area percentage of major tar compounds resulting from Y-zeolite catalytic treatment of producer gas tar.

Compound name	Molecular weight	Boiling point (°C)	Y-zeolite catalytic reaction temperature (°C)				
			500	550	600	650	700
Benzene	78	80	11.45	9.57	14.35	10.69	7.08
Toluene	92	110.6	13.63	11.19	12.15	16.93	45.04
Ethylbenzene	106	145	0.85	0.87	–	–	–
p-Xylene	106	138.3	1.31	1.80	1.94	2.95	–
o-Xylene	106	144.5	2.87	3.62	4.65	6.59	9.85
Benzene, (1-methylethyl)-	120	172.8	0.19	0.16	–	–	–
Indene	116	182	6.54	6.50	7.27	2.82	6.01
Methylindene	130	199	7.87	11.04	4.88	4.69	8.54
Naphthalene	128	217.9	4.27	6.39	6.54	7.90	23.48
2-Methylnaphthalene	142	241.1	3.01	5.84	4.88	5.66	–
1-Methylnaphthalene	142	244.7	2.10	5.88	4.33	2.61	–
4-Butyl-1,1'-biphenyl	210	318	2.54	–	–	–	–
Anthracene	178	339.9	4.50	10.33	6.96	–	–
Methylenephenanthrene	190	353	4.03	5.71	7.17	–	–
Fluoranthene	202	384	3.23	5.71	4.44	–	–
Pyrene	202	404	6.29	8.22	11.75	26.00	–
11H-benzo[b]fluorene	216	405	7.56	7.15	8.70	13.17	–
Pyrene, 1-methyl-	216	405	6.25	–	–	–	–
Acepyrene	226	448	11.48	–	–	–	–

Table 4
Comparison of tar reduction efficiency and producer gas heating value under different treatment methods.

Feedstock	Primary treatment			Secondary treatment			Tar reduction (%)	Gas heating value (MJ Nm ⁻³)	Ref.
	Reactor type	Bed material	Temperature (°C)	Reactor type	Bed material	Temperature (°C)			
Rubber wood blocks	Downdraft fixed bed gasifier	Wood	940	RF thermal and catalytic fixed bed reactor	SiC	900–1200	50–91	4.72–5.76	Present study
Rubber wood blocks	Downdraft fixed bed gasifier	Wood	940	RF thermal and catalytic fixed bed reactor	SiC + Calcined Y-Zeolite	500–700	64–97	4.58–4.82	Present study
Rubber wood blocks	Downdraft fixed bed gasifier	Wood	940	RF thermal and catalytic fixed bed reactor	SiC + Calcined Dolomite	700–900	65–97	4.48–5.06	Present study
Paper-reject sludge	Catalytic fixed bed gasifier	Zeolite	900	Three catalytic hot-gas cleaning reactors, filled with zeolite, dolomite and activated carbon		250	94.1–99.2	–	Chiang et al. (2013)
Chopstick	Fluidized bed gasifier	Sand	600 700 800	–		–	–	9.40 ^a 11.91 ^a 12.55 ^a	Chiang et al. (2012)
		CaO	600					10.22 ^a	
		Clay	600					9.56 ^a	
		Zeolite	600					10.12 ^a	
Cedar biomass	Updraft gasifier	Biomass	–	Tubular thermal reformer		650 750 850 950	Base 16 – 97	9.3 ^a 10.4 ^a 11.3 ^a 12.1 ^a	Aljbour and Kawamoto (2013)
Coal	Fluidized bed pyrolyzer	Coal	850	Downdraft fixed bed gasifier		– 1000 1100 1200	Base 59 66 73	2.93 3.23 3.46 3.57	Zeng et al. (2011)
High density polyethylene (HDPE)	Conical spouted bed reactor	Sand	800	–		–	Base	12.82 ^a	Erkiaga et al. (2013)
			850					46	
			900					32	
Jack Pine Sawdust	Fixed bed microreactor	Biomass	850	Catalytic fixed bed microreactor	Canadian dolomites	650 700 750 800	46 60 66 80	–	Gusta et al. (2009)
EFB	Bubbling fluidized bed gasifier	Sand	650	–	–	–	–	3.27	Lahijani and Zainal (2011)
			1050					–	
Sawdust	Bubbling fluidized bed gasifier	Sand	650	–	–	–	–	5.37 3.86	Lahijani and Zainal (2011)
			1050					–	
Sewage sludge	Bubbling fluidized bed gasifier	Sand	770–799	Tar-cracking fixed bed reactor	No additive	796	Base	5.87 7.55 ^b	Mun et al. (2013)
					Calcined zeolite	795		49.2	
					Calcined dolomite	794		85.5	
					Calcined olivine	794		50.4	
Sewage sludge	Bubbling fluidized bed gasifier	Calcined dolomite	798–801	Tar-cracking fixed bed reactor	No additive	802		78.6 7.16 ^b	Mun and Kim (2013)
					Calcined dolomite	805		86.3	
Mixed plastic wastes	Bubbling fluidized bed gasifier	Calcined dolomite	798–801	Tar-cracking fixed bed reactor	No additive	807		27 7.51 ^b	Cho et al. (2013)
					Activated carbon	789		38	
Coir pith	Fluidized bed gasifier	Sand	600 680	–	–	–	–	8.04 ^b 3.04 3.67	Subramanian et al. (2011)

(continued on next page)

Table 4 (continued)

Feedstock	Primary treatment		Secondary treatment			Tar reduction (%)	Gas heating value (MJNm ⁻³)	Ref.
	Reactor type	Bed material	Temperature (°C)	Reactor type	Bed material			
Rice husk	Fluidized bed gasifier	Sand	750	-	-	-	4.23	Subramanian et al. (2011)
			650				3.75	
			750				4.10	
Saw dust	Fluidized bed gasifier	Sand	870	-	-	-	4.61	Subramanian et al. (2011)
			650				3.47	
			750				4.21	
			850				4.54	

^a N₂ free basis.

^b HHV calculated based on Eq. (2).

Fig. 5 also shows the different formation of gases with increasing catalytic reaction temperature. It was found that at temperatures of 500 to 600 °C, the yield of CO and H₂ slightly increase whilst CO₂ and CH₄ decrease. This result is attributed to the water gas reaction and dry methane reforming activity. In addition, the decrease of CO₂ content at the corresponding temperature and then increases with the increase of catalytic reaction temperatures is also due to CO₂ adsorption by Y-zeolite as a catalyst at a certain amount. The physical ability of Y-zeolite on CO₂ adsorption has been demonstrated in a previous study (Kuo et al., 2013). Y-zeolite has good performance on CO₂ adsorption at ambient or moderate temperatures but significantly reduces at high temperatures (Fisher et al., 2011). The result in this study also shows that above 600 °C, the formation of CH₄ and H₂ tended to increase but CO shows the opposite formation. The decrease of CO content at high catalytic reaction temperature with Y-zeolite is mainly caused by the progressive activity of water gas shift and methanation reactions. Tar cracking reactions promoted by the Y-zeolite catalyst also contributes to the formation of valuable gases at high reaction temperature. As shown in Fig. 6, at temperature of 700 °C the highest tar and particle conversion efficiencies were obtained. It was found that the conversion efficiencies of both tar and particle were about 97%, corresponding to the tar concentration of about 55 mg Nm⁻³ and particle concentration of 11 mg Nm⁻³. The large surface area, pore size and acidic nature of Y-zeolite support cracking and reforming reactions of tar and particle under the condition investigated. This leads to the improvement of producer gas quality, where the gas heating value increases by 8% at the highest temperature experiment.

Tar species contained in producer gas after catalytic treatment using Y-zeolite is given in Table 3. It was found that only a small portion of tar compounds contained in raw producer gas was not detected at catalytic reaction temperature of 500 °C. This finding is slightly different to the detected tar species in the case of dolomite at 700 °C in which phenanthrene, styrene and chrysene were not identified in the case of Y-zeolite at 500 °C. In addition, most of the heavy PAHs were decomposed at reaction temperature of 500 °C, meaning that the Y-zeolite catalyst inhibits the formation of high-ring tar compounds (Chiang et al., 2013). This activity could be due to Y-zeolite catalyst contained sufficient acidic active sites on its surface thereby accelerates tar cracking reaction (Buchireddy et al., 2010). Increasing the catalytic reaction temperature up to 700 °C, it can be seen that the catalytic activities of Y-zeolite increased significantly. At this condition, benzene, toluene, o-xylene, indene, methylindene and naphthalene were the only major compounds identified.

3.3. Comparison of thermocatalytic treatment of tar

Experimental results on producer gas quality after treatment via thermal and catalytic treatment processes were compared to the findings of other researchers reported in the literatures. The results are summarized and presented in Table 4. In this case, the producer gas quality was characterized by the gas heating value and conversion efficiencies of tar and/or particle under different treatment methods. It can be observed that generally the gas heating value and tar reduction efficiency increased with the increase of temperature. The use of catalyst has also a positive effect on improving the gas heating value and tar conversion efficiency. However, these results might be different under excessive amount of steam, air and/or oxygen. This behavior occurs strongly when the heat is directly supplied to the reactor using an excess of air or oxygen (high ER) to raise the temperature through exothermic reactions. In this case, the gas heating value decreased although tar and particles reduction efficiency increased significantly.

4. Conclusions

The performance of RF tar thermocatalytic treatment system was investigated. Temperature plays a crucial role for tar and particle conversions under the investigated conditions. Thermal treatment produces higher heating value of 5.76 MJ Nm⁻³ at 1200 °C. Both dolomite and Y-zeolite offer better tar and particles conversion efficiencies of around 97%. Even at higher temperature of thermocatalytic cracking benzene, naphthalene and toluene were still found. The presence of reforming products, water and particulates in the producer gas has a major impact on upgrading producer gas quality.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2013.10.010>.

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