Removal of Tar from Biomass Gasification Process by Steam Reforming over Nickel Catalysts

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Tar steam reforming (TSR) is a very attractive technique for tar removal. It converts high molecular weight hydrocarbons of tar into smaller gas products including H_2, CH_4, CO and CO_2. Preliminary research focuses on simulation of tar steam reforming. It was assumed to be at thermodynamic equilibrium and the calculations were performed using Aspen Plus Program. The simulation results help understand the effect of operating condition and identify suitable operating conditions (reaction temperature, S/C ratio) for the experimental tar steam reforming. Representative tar consisted of $C_{10}H_8$, C_7H_8, C_6H_6O and $C_{16}H_{10}$ whose compositions varied with temperatures of biomass gasification (700-800 ^{0}C). The experimental study of the tar steam reforming reaction was carried out at different temperatures (450-650 ^{0}C), S/C ratios (1-5), type of supports (Al_2O_3, CaO and MgO) and %metal loading of a nickel catalyst (10, 15 and 20 %). The experimental results follow the trends observed from the simulations that the reaction at high temperature and S/C ratio produce more hydrogen content. 20 %Ni/Al_2O_3 was reported as a suitable catalyst which offered stable and efficiency activity for tar steam reforming.

1. Introduction

Nowadays, depletion of fossil fuel sources and environmental problems such as global warming are the world's major issues. However, due to the growth of the world's population, the energy demand is still continuously increasing. Therefore, a number of current researches have been focusing on renewable energy in order to replace the conventional fossil fuel-based energy. In this study the focus is on biomass gasification which is expected to be a real commercial process. Biomass gasification has attracted huge interest by producing a gas rich in H_2 and CO (Saxena et al., 2008) which can be used as a gaseous fuel for electricity generation or fuel cell (Devi et al., 2003).

The major problem of biomass gasification is that the produced gas usually contains unacceptable levels of tar causing process-related problems. Tar from fuel gas condenses at low temperatures, thus blocking, fouling corrosion, erosion and abrasion of process equipment such as engines and turbines. Tar is a complex mixture of aromatics which composition of biomass gasification tars as reported (Milne et al., 1998) includes benzene, toluene represent one-ring aromatic hydrocarbons, naphthalene represent two-ring aromatic hydrocarbons, etc. There are 6 classes of tar based on the tar classification system developed (Bergman et al., 2002). Each class is also divided into different types of tar according to its different nature. Comprehensive significant compounds in tars, it has been grouped as a mixture of four compounds with each compound representing a specific class of compounds and the composition equal to group in actual tars is used. The species and their amounts that were chosen to represent tars are toluene representing all the one-ring compounds, naphthalene representing two-ring compounds, phenol representing phenolic and other heterocyclic compounds, pyrene representing three-rings and higher compounds (Singh et al., 2005).
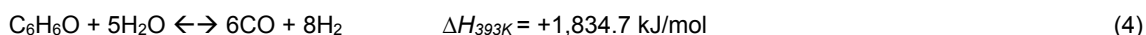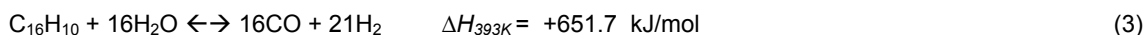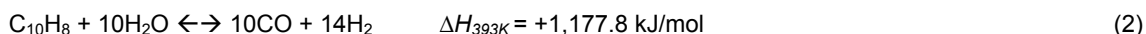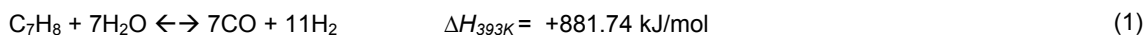
Several methods for tar removal are possible (Stassen et al., 2002): tar removal by physical processes (Milne et al., 1998) (e.g. filters, scrubbers, wet electrostatic precipitators and cooling tower (Vivanpatarakij et al., 2013) and chemical processes (e.g. thermal cracking, catalytic cracking and catalytic reforming). Tar steam reforming is a very attractive technique for tar removal, converted into useful gas containing H_2, CH_4, CO and CO_2. Several kinds of catalytic reforming have been studied, developed and used in removal of tar, such as mineral resource: dolomites, magnesites, zeolites, olivine, mayenite mineral, alkali metal

catalysts, Ni-based catalysts and novel metal catalysts (Han et al., 2008). However, it was reported that these catalysts have many of the problems, although they showed good activity in removal of tar. Without a pretreatment, natural mineral catalysts suffer from low activity and stability. Nickel-based catalysts have shown high activities for reforming of biomass gasification tar. When being used as the secondary catalysts, the supported nickel catalysts could attain nearly complete decomposition of both tar and ammonia decomposition (Han et al., 2008). However, Ni catalyst suffers from coke deposition, leading to deactivation of the catalysts (Dayton et al., 2002). $Ni/CeO_2(75 \%)-ZrO_2(25 \%)$ showed the most pronounced catalytic performance in the steam reforming of benzene and showed strong resistance to coke deposition. Its activity is superior to a commercial Ni catalyst (Park et al., 2010). Steam reforming of toluene as a tar model compound using Ni/olivine catalyst was reported to have much higher activity and selectivity towards syngas than olivine alone (Swierczynski et al., 2007). Three Ni-based catalysts (ICI46-1, Z409 and RZ409) were proven to be effective in eliminating heavy tars (Zhang et al., 2004). Apart from Ni-based catalysts, there have been other catalysts developed for tar removal. The conversion rate of tar catalyzed by dolomite was difficult to reach or exceed 90-95 %, although dolomite could reduce the tar in syngas (Xiaodong et al., 2003).

In this work, tar removal and hydrogen production from steam reforming was investigated. This study focused on finding suitable condition for the highest amount of H_2 yield and tar conversion by preliminary simulations using Aspen Plus program. It is also aimed at finding a suitable catalyst to be used in the steam reforming of tar for different mixtures of $C_{10}H_8$, C_7H_8, C_6H_6O and $C_{16}H_{10}$ as model compounds of tar at different temperatures of biomass gasification. The effect of operating parameters on the hydrogen production is also investigated.

2. Experimental

Figure 1 show the tar compositions at different temperatures, used in this study (Brage et al., 1996). The steam reforming reactions of tar representative compounds are given in Eqs (1-4). The methane steam reforming (Eq (5).) and water gas-shift reaction (Eq (6).) were also considered.

$$C_7H_8 + 7H_2O \leftrightarrow 7CO + 11H_2 \qquad \Delta H_{393K} = +881.74 \text{ kJ/mol} \tag{1}$$

$$C_{10}H_8 + 10H_2O \leftrightarrow 10CO + 14H_2 \qquad \Delta H_{393K} = +1,177.8 \text{ kJ/mol} \tag{2}$$

$$C_{16}H_{10} + 16H_2O \leftrightarrow 16CO + 21H_2 \qquad \Delta H_{393K} = +651.7 \text{ kJ/mol} \tag{3}$$

$$C_6H_6O + 5H_2O \leftrightarrow 6CO + 8H_2 \qquad \Delta H_{393K} = +1,834.7 \text{ kJ/mol} \tag{4}$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H_{393K} = +209.44 \text{ kJ/mol} \tag{5}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_{393K} = -40.01 \text{ kJ/mol} \tag{6}$$

The reactants used for the reaction study are $C_{10}H_8$, C_7H_8, C_6H_6O and $C_{16}H_{10}$ (Analytical grade). The catalytic tests were performed in a flow system shown diagrammatically in Figure 2. The setup consists of three sections. The first section is for preparing a tar model compounds with a controlled composition and flow rate. The second section is the reactor system including the fixed bed reactor and temperature control device. The third section is the analysis system where the gases from the reactor are analyzed by gas chromatography (GC). The instruments used in this system are listed and explained as follows.

The experiments were carried out at atmospheric pressure in a fixed-bed quartz reactor (9 mm diameter and 500 mm length) placed in a furnace with a temperature controller. The catalyst bed (0.3 g) was diluted with silicon carbide (1.0 g) by quartz wool in the uniform temperature zone (GHSV = 1,900 h^{-1}). The temperature was monitored by a thermocouple placed outside of the reactor. Two motorized syringe pumps were used to introduce the liquids: water and mixture tar model compounds including $C_{10}H_8$, C_7H_8, C_6H_6O and $C_{16}H_{10}$ which are then evaporated and carried to the reactor by a nitrogen flow controlled by a mass flow controller. The different operating parameters were studied as summarized in Table 1.

Table 1: Experimental condition for catalytic reaction.

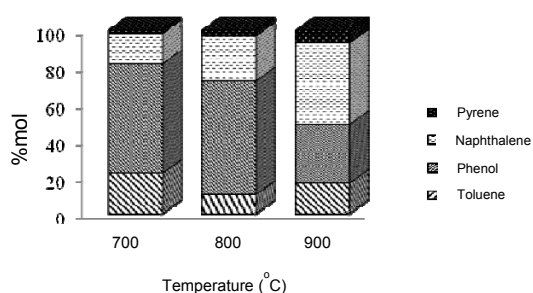| Composition Tar		N_2 flow rate	Tar flow rate	Temperature	S/C	Pressure
N_2 balance	$C_{10}H_8$, C_7H_8,C_6H_6O, $C_{16}H_{10}$	(20 mL/min)	(0.06 mL/min)	450-650 ^{0}C	1 – 5	Atmosphere

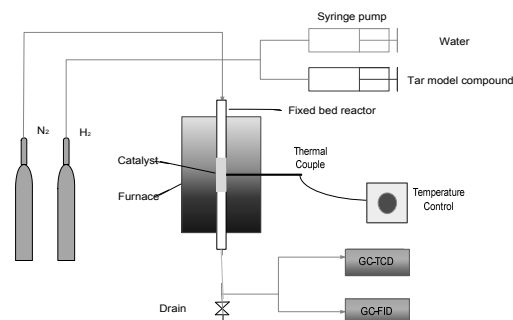Figure 1: Major compounds chosen to represent tar model compound.

Figure 2: Schematic of the experimental system.

3. Results and Discussions

3.1 Catalytic performance on tar steam reforming

3.1.1 Effect of support and %Ni loading

Figure 3.a shows the H_2 yields. The support of Al_2O_3 offers the highest %H_2 yield of 13 %. From the result, it was clear that Al_2O_3 offers superior reactivity to the CaO and MgO supports. Figure 3.b, the results indicate that at 15 %Ni/Al_2O_3 offers the highest %H_2 yield compared to 10 %Ni/Al_2O_3 and 20 %Ni/Al_2O_3. It should be noted that after 2 h reaction, for 10 %Ni/Al_2O_3 H_2 concentration decreased rapidly. Considering %H_2 yield (Figure 3.b), it was found that 20 %Ni/Al_2O_3 showed the largest value of %H_2 yield.
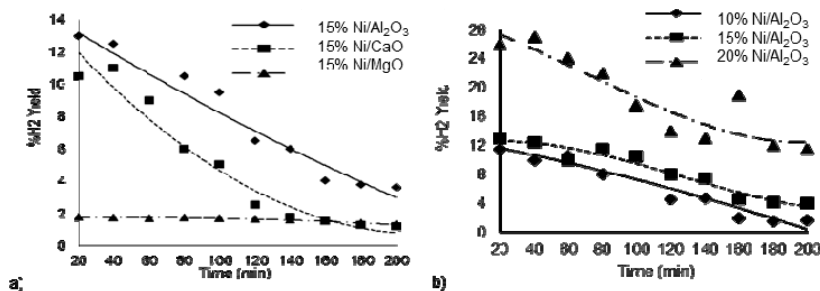

Figure 3: a) Effect of catalyst support on the H_2 yield from tar steam reforming, b) effect of %Ni loading on % H_2 yield of tar steam reforming (T = 450 ^{0}C, S/C ratio:5).
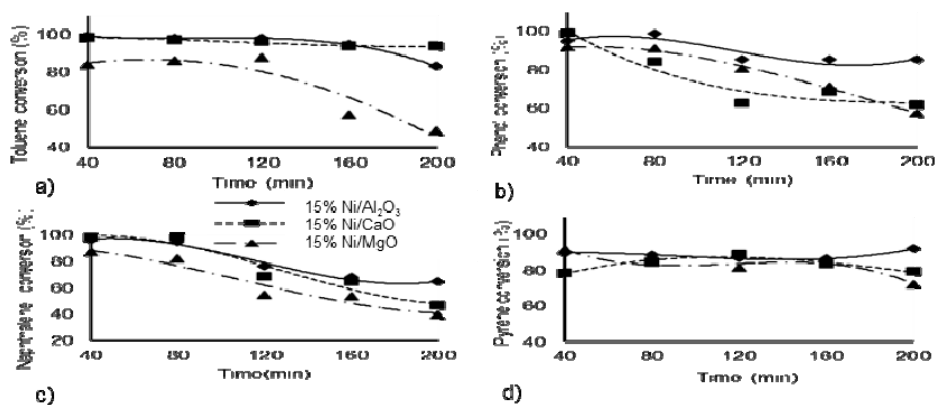

Figure 4: Tar conversion of supported catalysts on the tar steam reforming of a) C_7H_8, b) C_6H_6O, c) $C_{10}H_8$, and d) $C_{16}H_{10}$, (T=450 ^{o}C, S/C ratio = 5).

The tar conversions on various supported catalyst and %Ni loading are shown in Figure 4 and 5, respectively. It was found that 15 % Ni/MgO gives the lowest tar conversion. The 20 %Ni/Al$_2$O$_3$ has almost the highest tar conversion of most tar components. Among different tar components, naphthalene conversion is the lowest probably because naphthalene has the most complex structure and therefore it is the most difficult to be decomposed.
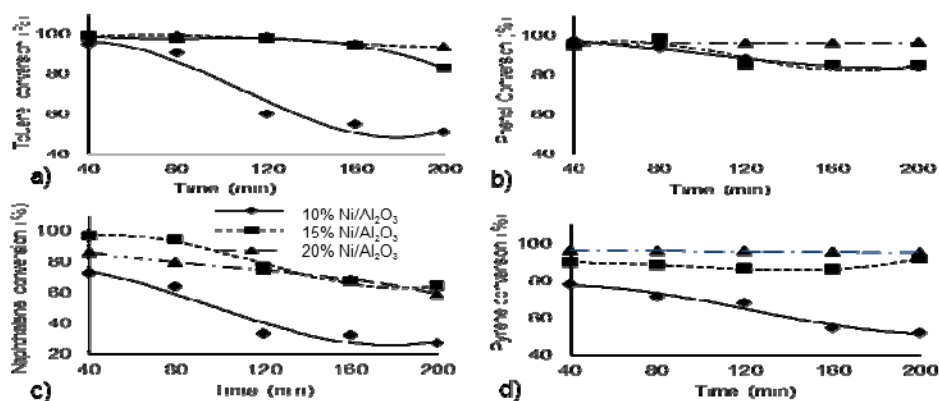

Figure 5: Tar conversions of Ni/Al$_2$O$_3$ at different %Ni loadings of a) C$_7$H$_8$, b) C$_6$H$_6$O, c) C$_{10}$H$_8$, and d) C$_{16}$H$_{10}$, (T= 450 ^{o}C, S/C ratio = 5).

3.1.2 Effect of reaction temperature and S/C ratio

Figure 6.a show the product compositions of the tar steam reforming of 20 %Ni/Al$_2$O$_3$ at 450-650 ^{0}C and S/C ratio of 5. The results indicated that higher H$_2$ concentration (%mol) and H$_2$ product (mol/min) was achieved with increasing reaction temperature. At T = 650 ^{0}C, the value of the %H$_2$ yield is the largest (about 61 %). This is because the tar steam reforming is an endothermic reaction and, therefore, the reaction is favourable at high operating temperature due to both the thermodynamics and the improved kinetics at elevated temperature. The results on tar conversions are shown in Figure 7. All tar components could be better decomposed at higher temperatures. The conversions slightly decreased with increasing temperature except naphthalene which is the most difficult component with most difficult to be decomposed.
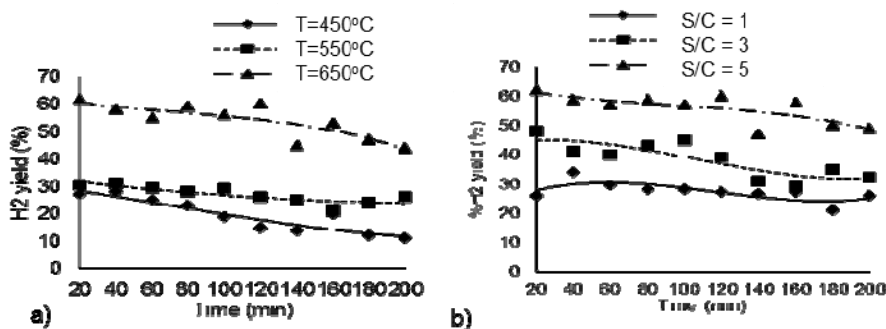

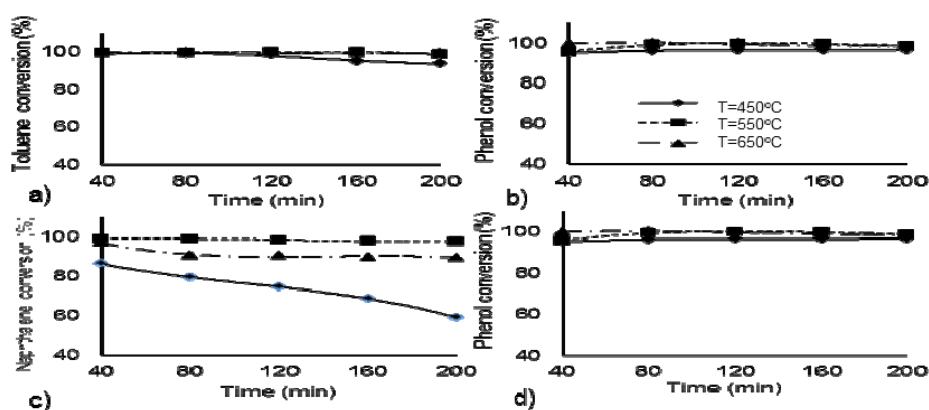*Figure 6: a) Effect of reaction temperature (S/C ratio = 5) and b) Effect of S/C ratio on %H$_2$ yield of tar steam reforming of 20 %Ni/Al$_2$O$_3$ (T = 650 ^{0}C).*

Figure 7: Tar conversions of 20 %Ni/Al$_2$O$_3$ catalyst on the tar steam reforming at various reaction temperatures of a) C$_7$H$_8$, b) C$_6$H$_6$O, c) C$_{10}$H$_8$, and d) C$_{16}$H$_{10}$, *(S/C ratio =5).*

The effect S/C ratio 1-5 on tar steam reforming was performed using 20 %Ni/Al$_2$O$_3$ at 650 ^{0}C. Increasing S/C ratio resulted in increasing H$_2$ product as well as %H$_2$ yield. The observed H$_2$ concentration and H$_2$ yield (Figure 6.b) varied in ranges of 74-85 and 25-62 %mol, respectively. The highest H$_2$ product was observed at the S/C ratio of 5. Additional steam in the feed could help to improve the conversions of all tar components (Figure 8). The increased S/C ratio did not only promote the steam reforming but also the water gas shift reaction, resulting in higher H$_2$ concentration and yield.
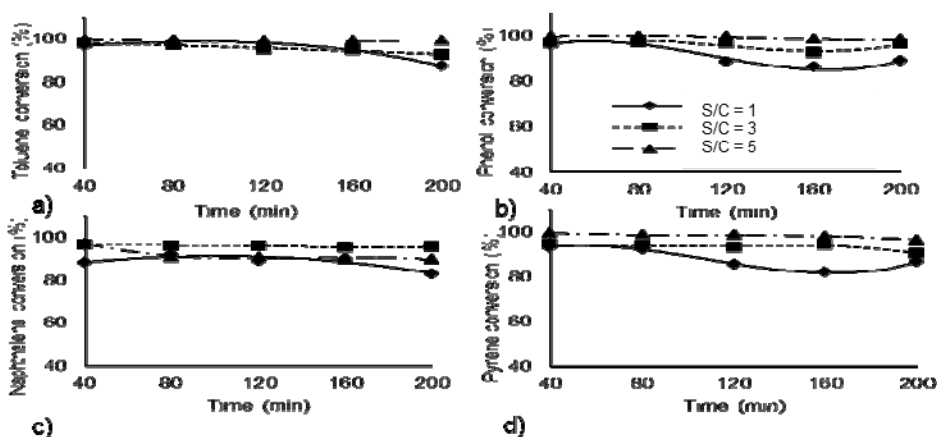

Figure 8: Tar conversions of 20 %Ni/Al$_2$O$_3$ catalyst at various S/C ratios of a) C$_7$H$_8$, b) C$_6$H$_6$O, c) C$_{10}$H$_8$, and d) C$_{16}$H$_{10}$ *(T = 650 ^{0}C).*

4. Conclusions

The results of catalytic reactions in tar steam reforming reaction indicate that tar was favorably converted to synthesis gas (H$_2$, CO$_2$, CH$_4$ and CO) at high temperatures and S/C molar ratio. The composition of tar derived from biomass gasification at 800 ^{0}C offers the highest H$_2$ content. The support Al$_2$O$_3$ allows the nickel loading into pore volume and surface area. When the %Ni loading was increased, the Ni distribution on surface area of alumina support becomes better. From experimental results, high temperature operation and S/C ratio are favorable to hydrogen production. Then, 20 %Ni/Al$_2$O$_3$ catalyst has good stability and suitability in tar steam reforming reaction at 650 ^{0}C and S/C ratio of 5.

5. Acknowledgement

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