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Catalytic Decomposition of Biomass Tars at Low-Temperature

Le Duc Dung, Kayoko Morishita and Takayuki Takarada

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1. Introduction

Tar is a viscous black liquid derived from pyrolysis of organic matter as well as a complex mixture of hydrocarbons. The presence of tar in product gas may cause blockage and corrosion of equipment and be responsible for fouling or reducing overall efficiency of processes. By far, tar removal is the most problematic during biomass gasification. Hence, the successful implementation of gasification technology for gas engine, gas turbine or fuel cell based power projects depends much on the effective and efficient removal or conversion of tar from the product gas. Beside that the catalytic steam reforming tar is one of the most promising methods to suppress the problems. Biomass product gas is usually low high heating value; therefore enhancement of product gas quality is other important target. We propose a research topic that use of nickel loaded brown coal char as a new catalyst for decomposing tar from biomass gasification in fluidized bed gasifier. The method is promising to achieve some advantages of low cost by use of low rank coal as catalyst support material, high catalyst activity and enhancement of product gas quality. Yallourn brown coal has been selected for preparing catalyst support. The coal is low rank with high moisture content, low heat value and high oxygen content. It is hard to use for generating energy. However, it has many outstanding features such as less ash and sulfur content, and including abundant of oxygen–containing functional groups such as carboxyl and phenol groups which are available for ion–exchange with metals. In this research work, a nickel loaded brown coal char (Ni/BCC) was prepared by ion–exchange method, dried at 380 K in nitrogen for 24 h, and then pyrolysed at 923 K in nitrogen for 90 min. The works have been carried out is that using nickel loaded brown coal to decompose tar in pyrolysis and steam gasification process. It was carried out in a two–stage fixed–bed reactor and a lab scale fluidized bed gasifier under mild conditions (temperature, steam, space velocity, operation time). Inside of gasifier is constructed by two beds, the primary one is a fluidized bed with sand, and the second one is a catalyst bed. The new catalyst has shown high catalytic
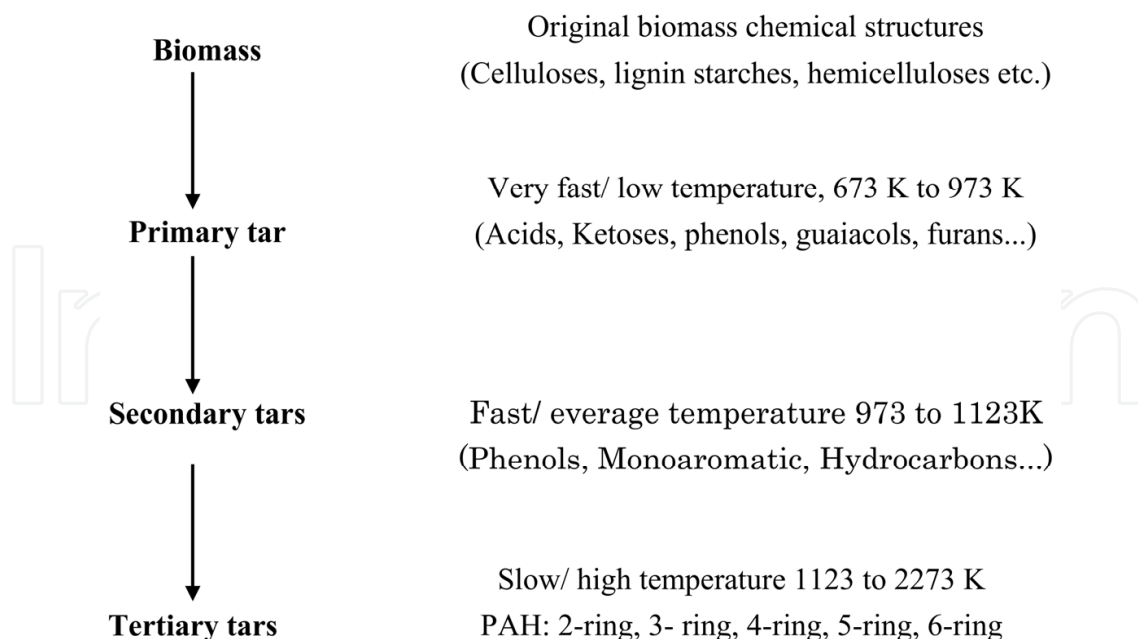
activity and stable activity and given the high quality of product gas in presence of steam, approximately 90% of biomass tar was decomposed and useful gas components (CH_4, CO, and H_2) yields were higher than those of Ni/Al_2O_3 catalyst. Ni/BCC catalyst was characterized and exhibited good dispersion of nickel particles, ultra–fine Ni less than 15 nm and having a large surface area about 350 m^2/g. Moreover, at the end of catalyst life span, the catalyst can be disposed of simply by gasifying/burning the coal char, during which the energy value of the char support can be recovered. Also, the agglomerated nickel residues could be used as functional materials of powder metallurgy and battery development. The general results suggest that the Ni/BCC catalyst offers a potential to be used as a tar steam reforming catalyst in biomass gasification.

1.1. Tar and tar removal

There are still many questions related to tar and the problems they may cause. Tar is a viscous black liquid derived from pyrolysis of organic matter as well as a complex mixture of hydrocarbons [1]. Various research groups are defining tar differently. In the EU/IEA/US-DOE meeting on tar measurement protocol held in Brussels in the year 1998, it was agreed by a number of experts to define tar as all organic contaminants with a molecular weight larger than benzene [2]

The presence of tar in product gas may cause blockage and corrosion of equipment and be responsible for fouling or reducing overall efficiency of processes. Tar is formed when biomass is heated the molecular bonds of the biomass break; the smallest molecules gaseous, the larger molecules are called primary tars. These primary tars, which are always fragments of the original material, can react to secondary tars by further reactions at the same temperature and to tertiary tars at high temperature [3, 4, 5, 6] Figure 1 show tar is quite complex and hard to decompose. By far, tar removal is the most problematic during biomass gasification. Hence, the successful implementation of gasification technology for gas engine/turbine based power projects depends much on the effective and efficient removal/conversion of tar from the producer gas. Up to now, a great amount of work concerning tar reduction or reforming has been reported with abundant technologies to remove tar from biomass product gas.

J. Han, and H. Kim had divided tar removal methods into five groups: mechanical methods (using cyclone, filters ceramic), granular beds, Electrostatic precipitators and Scrubbers; self-modification, selecting optimal operation parameters for gasifier or using a low tar gasifier; Catalytic cracking; Thermal cracking and Plasma methods [5]. The review shows that the primary use of mechanism methods is to capture the fly ash or particles from product gas; the effect on tar removal is also very good. However, these methods only remove or capture the tar from product gases, while the energy in tar is lost. The self–modification and other methods can not only reduce the tar but also convert the tar into useful gases. The self–modification methods include: selecting better gasifer, and optimizing operation parameters. Tar reduced by modifying operation parameter is at the expense of reducing the heat value of gases. Catalyst cracking and thermal cracking are generally used to decompose or reduce tar though there are still some disadvantages. Plasma technology cannot only

Biomass   Original biomass chemical structures
                               (Celluloses, lignin starches, hemicelluloses etc.)

Primary tar   Very fast/ low temperature, 673 K to 973 K
                               (Acids, Ketoses, phenols, guaiacols, furans...)

Secondary tars   Fast/ everage temperature 973 to 1123K
                               (Phenols, Monoaromatic, Hydrocarbons...)

Tertiary tars   Slow/ high temperature 1123 to 2273 K
                               PAH: 2-ring, 3- ring, 4-ring, 5-ring, 6-ring

Figure 1. Formation of biomass tars and compounds formed

effectively remove fly ash, NOx and SO_2, but also sharply decrease the formation of tar during biomass gasification. In order to get highly efficient tar decomposition, the temperature of thermal cracking needs to be very high, which results in operating cost increase. Catalyst cracking can modify the composition of product gases at low temperature with high carbon conversion efficiency. Nevertheless, there still exists a short coming such as: the commercial Ni-based and alkali metal catalysts will be inactive by deposited carbon, and H_2S. The newly developed novel catalyst can overcome the disadvantages by use of expensive metals (Co, Pt, Ru, Pd and Rh), and also catalyst supports (Al_2O_3, Al, SiO, TiO_2, ZrO_2, MgO or WO_3) and perform tar removal with high and stable activity even under the presence of high concentration of H_2S in some cases. In order to satisfying both high and stable activity and good price, the development of catalyst meets the need to be continuing.

1.2. Catalysts

Due to the advantages of converting tar into useful gases and adjusting the compositions of product gases, catalyst cracking has been of interest since the middle 1980s. The simplified mechanism for catalyst tar reforming can be described as follows [7–9]. First, methane or other hydrocarbons are dissociatively adsorbed onto a metal site where metal catalyzed dehydrogenation occurs. Water is also dissociatively adsorbed onto the ceramic support, hydroxylating the surface. At the appropriate temperature, the OH radicals migrate to the metal sites, leading to oxidation of the intermediate hydrocarbon fragments and surface carbon to CO + H_2. David [9,10] summarized the criteria for catalyst as follows:

1.   the catalysts must be effective in removing tar;
2.   if the desired product was syngas, the catalysts must be capable of reforming methane;
3.   The catalysts should provide a suitable syngas ratio for the intended process;

4. the catalysts should be resistant to deactivation as a result of carbon fouling and sintering;

5. the catalysts should be easily regenerated.

6. The catalysts should be strong; and

7. the catalysts should be inexpensive.

Moulijn J.A. [11] has classified main causes of the deactivation into five reasons that are poisoning, fouling, thermal degradation (sintering, evaporation) initiated by the often high temperature, mechanical damage and corrosion/leaching by the reaction mixture. The deactivation phenomenon inside a catalyst particle is described on Figure 2 [11]. Among them, thermal degradation reason often occurs during catalyst reforming tar at relative high temperature (Figure 3).
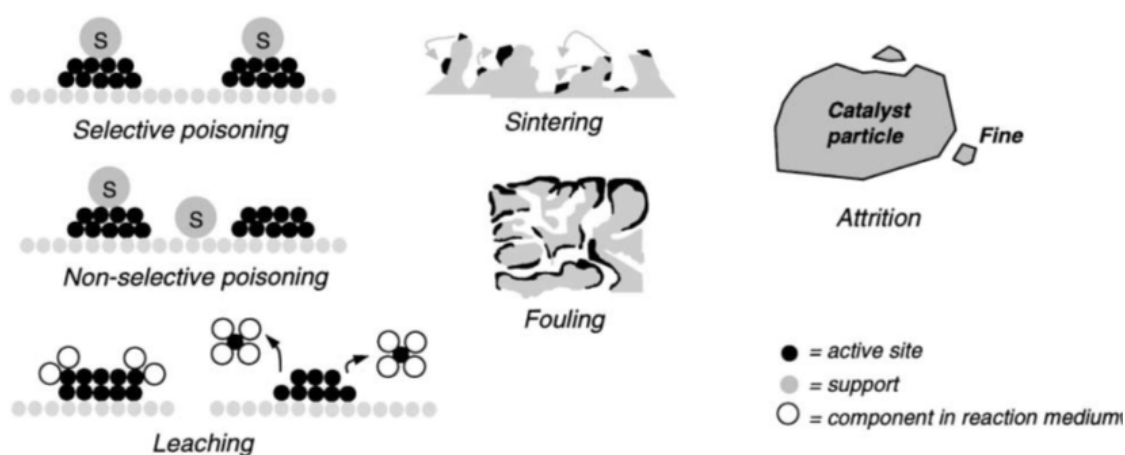
Figure 2. Major types of deactivation in heterogeneous catalysis
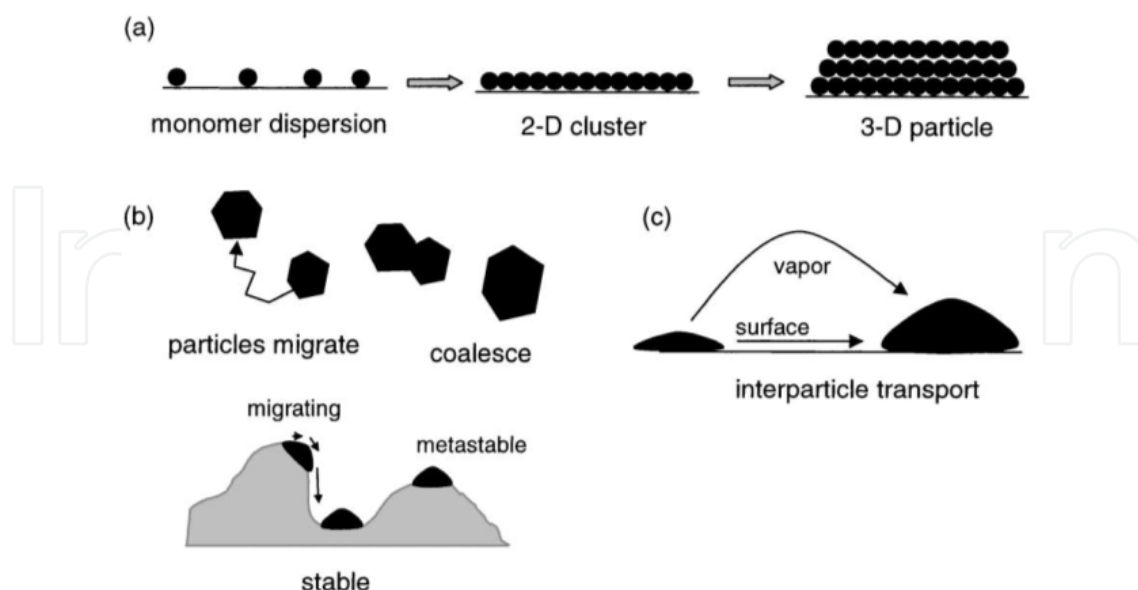
Figure 3. Schematic of the various stages in the formation and growth of particles from monomer dispersion ((a): Clusters of atoms (or small metal particles); two–dimensional clusters, and; three–dimensional particles; (b): Particles might move and coalesce; (c): Atoms move from one particle to another, either by volatilisation or by surface migration.)

Nikel based catalysts

Nickel has been developed with various promoters and carriers for decomposing tar and tar models [7–27].

Zhang [13] investigated tar catalytic destruction in a tar conversion system consisting of a guard bed and catalytic reactor. Three Ni based catalysts (ICI46–1, Z409 and RZ409) were proven to be effective in eliminating heavy tars (99% destruction efficiency). The experimental results demonstrated that space velocity (1500 –6000) had little effect on gas compositions, while increasing temperature boosted hydrogen yield and reduced light hydrocarbons (CH_4 and C_2H_4) formation, which suggested that tar decomposition was controlled by chemical kinetics.

Furusawa et al. [14] reported that 10 wt% Ni/MgO (873 K) catalyst showed the best performance. Nickel supported on silica was active for tar catalyst cracking methane at relatively low temperature (823 K) was described by Zhang [9].

Srinakruang et al.[15,16] has developed Ni/Dolomite as highly efficient sulphur and coking resistance catalyst, and reported that calcining at 500 ºC exhibited the most effective catalyst among Ni/SiO_2 and Ni/Al_2O_3; the poisoning effect was enhanced by increasing the reaction temperature and steam/C ratio; higher activity, durability and coking resistance.

Sato et al. [17], has developed $Ni–WO_3/MgO–CaO$ catalyst for naphthalene and toluene reforming. The results exhibited a better resistance to sulfur and coking catalyst; tar reforming to better than 90% and 100 h steady tar reforming operation (in H_2S) at 800–850 ºC.

Dou et al.[18] compared five catalysts on tar removal from fuel gases in a fixed–bed reactor. The Y–zeolite and NiMo catalysts were found to be the most effective about 100% tar removal can be achieved at 550 ºC. It was also observed that process variables like temperature and space velocity had very significant effect on tar removal.

Baker [19] also mentioned the phenomena in their experiments. In order to overcome the shortcoming of the commercial Ni–based catalyst, many Ni–based catalysts were developed.

Miyazawa et al. [20] has prepared Ni (Ni/Al_2O_3, Ni/ZrO_2, Ni/TiO_2, Ni/CeO_2 and Ni/MgO) catalyst to reformed tar in the partial oxidation (POT) and steam introduction. Results have been achieved: the order of the performance at 823 K was as follows: Ni/Al_2O_3 > Ni/ZrO_2 > Ni/TiO_2 > Ni/CeO_2 > Ni/MgO > no catalyst; Ni/CeO_2 showed smaller amount of coke than other catalysts; in the POT, much higher tar conversion and lower coke yield were obtained than that in SRT using fixed bed reactor.
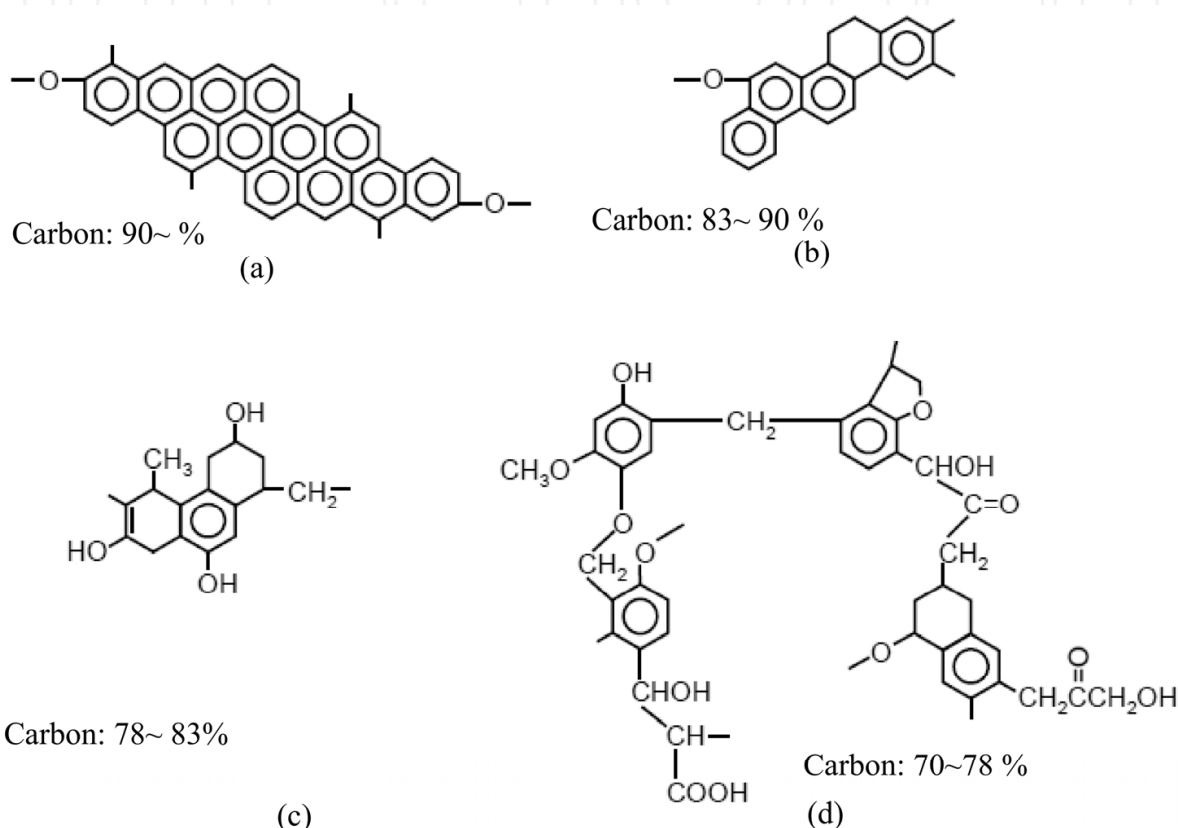
1.3. Catalytic brown coal gasification

It is very important to increase the thermal efficiency of coal conversion for not only protecting the limited coal resources but also reducing CO_2 and air pollutant emission. Steam gasification of coal is one of the most promising energy conversion technologies for producing hydrogen.

Brown Coal

Brown coal or lignite is a low rank with high moisture content of around 60 %, low heat value and high oxygen content. Therefore, it is hard to use for converted to useful energy. However, it is concluding many outstanding features such as less ash and sulfur content, and especially, including abundant of oxygen–containing functional groups such as carboxyl and phenol groups which are available for ion–exchange with metals. The structural unit of coal models is shown in Figure 4d.

Carbon: 90~ %

(a)

Carbon: 83~ 90 %

(b)

Carbon: 78~ 83%

(c)

Carbon: 70~78 %

(d)

Figure 4. Structural unit of coal models (a: anthracite coal; b: bituminous coal; c: bituminous coal; d: brown coal)

Catalytic coal gasification

Tomita [21, 22] has reported low temperature gasification of Yallourn coal catalysed by nickel. By the different way of prepared catalyst as usual like conventional impregnation methods, coal was mixed with an aqueous solution of hexamine nickel carbonate. This mixture gave a perfect homogeneous, catalyst bearing coal. Analysis product gas he found that the gases in the rapid stage of char gasification at 723 K presented mainly hydrogen and carbon dioxide. The study demonstrates the first time that nickel catalyst can enhance gasification reactivity in a similar manner as observed for activate carbon.

Tomita [23, 24] continued to carry out nickel brown coal gasification with various gasification conditions such as amount weight of nickel loaded on coal, various

temperatures. The good results exhibited carbon conversion reached 85%, with 30 min for steam gasification at low temperature as 723 K.

Ohtsuka [25] reported calcium catalysed steam gasification of Yallourn brown coal with the same way of preparation catalyst as Tomita have done. The results also showed that high activity for calcium catalyst steam gasification of brown coal.

Takarada [26] investigated catalyst steam gasification of coal by mixing of K–exchange brown coal. The results gave evident that rate of enhancement of K–exchange Yallourn coal by physical mixing method is independent of the caking property of higher rank coal; Potassium is a highly suitable catalyst for catalytic gasification.

Recently, Miki [27] also carried out pyrolysis and gasification of coal which was loaded Ni by ion– exchanged method, and again proved nickel loaded brown coal has a high activity in coal gasification.

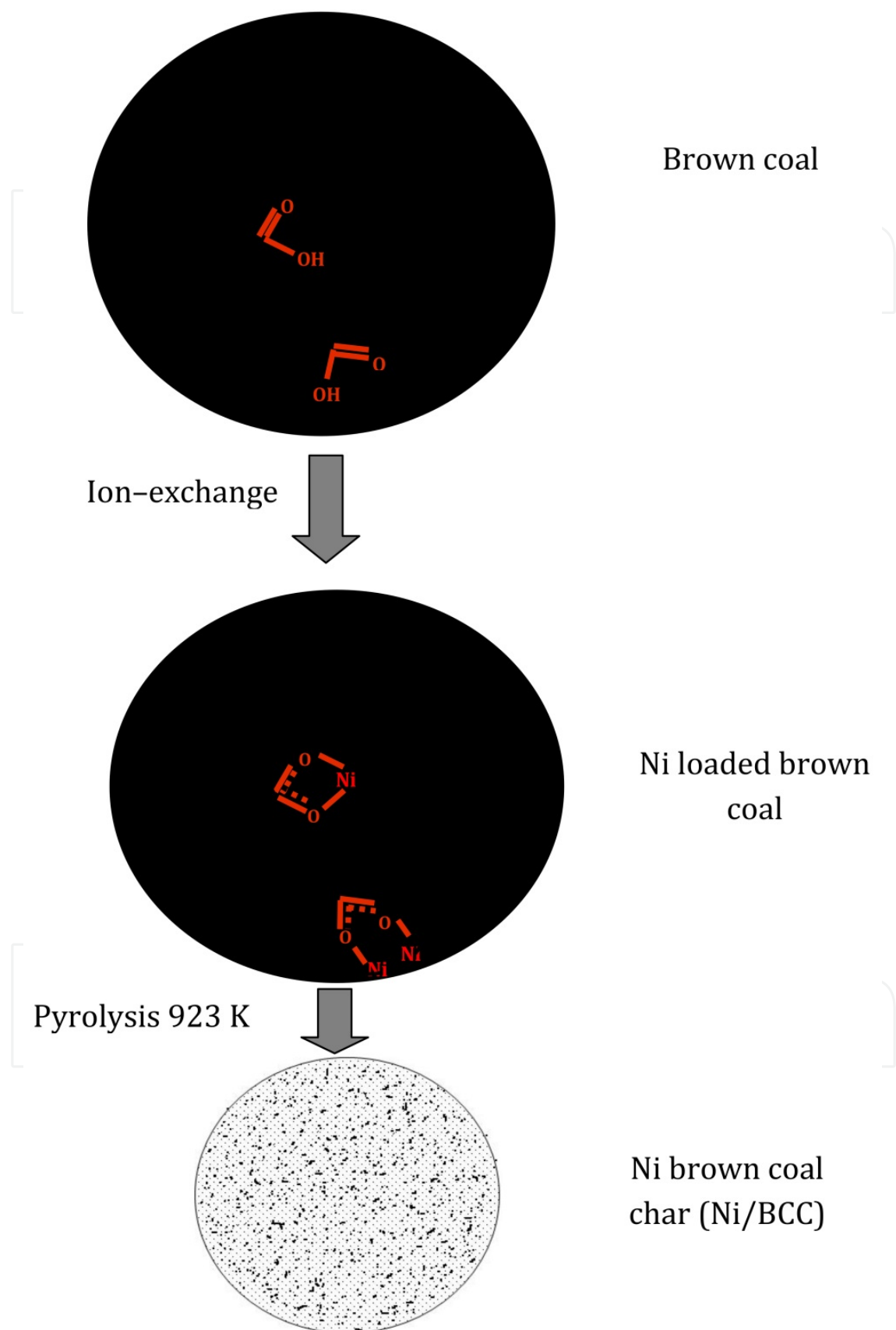# 2. Nickel catalyst preparation

2.1. Ni/BCC catalyst

The procedure of ion exchange is shown in Figure 5 and Figure 6. Yallourn (YL) coal char was used as catalyst support. YL coal (Australian brown coal) received in the form of briquettes. The coal was crushed, sieved to a particle size range of 1 – 2 mm in diameter, and then dried at 380 K for 12 h. The nickel addition to the coal matrix was achieved by ion–exchange with a solution of basic hexa ammine nickel carbonate $(NH_3)_6NiCO_3$ (Figure 5, 6). The coal was mixed with the $(NH_3)_6NiCO_3$ solution for 24 h and then recovered by filtration. The recovered solid was washed with distilled water and filtered again. Then, the washed solid was dried under N_2 flow at 380 K for 24 h. Last, raw catalysts were produced.

Catalysts was characterized by powder X–ray diffraction on XRD; M03XHF22, Mac Science Co., Ltd, using CuKα radiation(40 kV, 30 mA) in order to identify the potential evolution of the crystalline phases during catalyst pyrolysis tests. The diffractograms were recorded a step time of 10 sec. SEM analysis was applied to study the surface structure of Ni/BCC catalyst (FE–SEM; JSM–6700F, JEOL Datum Ltd.). An atomic absorption flame emission spectrophotometer (AA–6400F, Shimadzu Corp.) was used to examine the amount of Ni on raw Ni/BCC (Ni 9 ± 1%–dry). After pyrolyzing with nitrogen gas at 923 K for 90, its weigh loss is approximately 54 %, and therefore, nickel loaded in coal char could be estimated 19.6 ± 2%–char base. The intimacy of the contact between coal char and catalyst was so effective that the reactivity was considerably higher than those prepared by a conventional impregnation method [21–24]. Nitrogen adsorption characterization of catalysts was performed on equipment for automatic gas and vapor adsorption measurement (BELSORP–max, BEL Japan Co. Ltd.). Prior to adsorption measurement, the catalysts were degassed at 573 K for 3 h under a dynamic vacuum. The surface areas of fresh catalysts (Ni/BCC), which were obtained after pyrolysis of raw Ni/BCC at 923 K for 90 min is 350 m^2/g [28,29].

$$NiCO_3 2Ni(OH)_2 4H_2O, (NH_4)_2CO_3, \text{Ammonia}$$
solution and distilled water

$(NH_3)_6NiCO_3$

Distilled water

$(NH_3)_6NiCO_3$ Solution (pH =11)

Brown coal

Stirring (24 h)

Filtration

Washing (distilled water)

Dry (380 K, 24 h, in N_2)

Nickel loaded brown coal
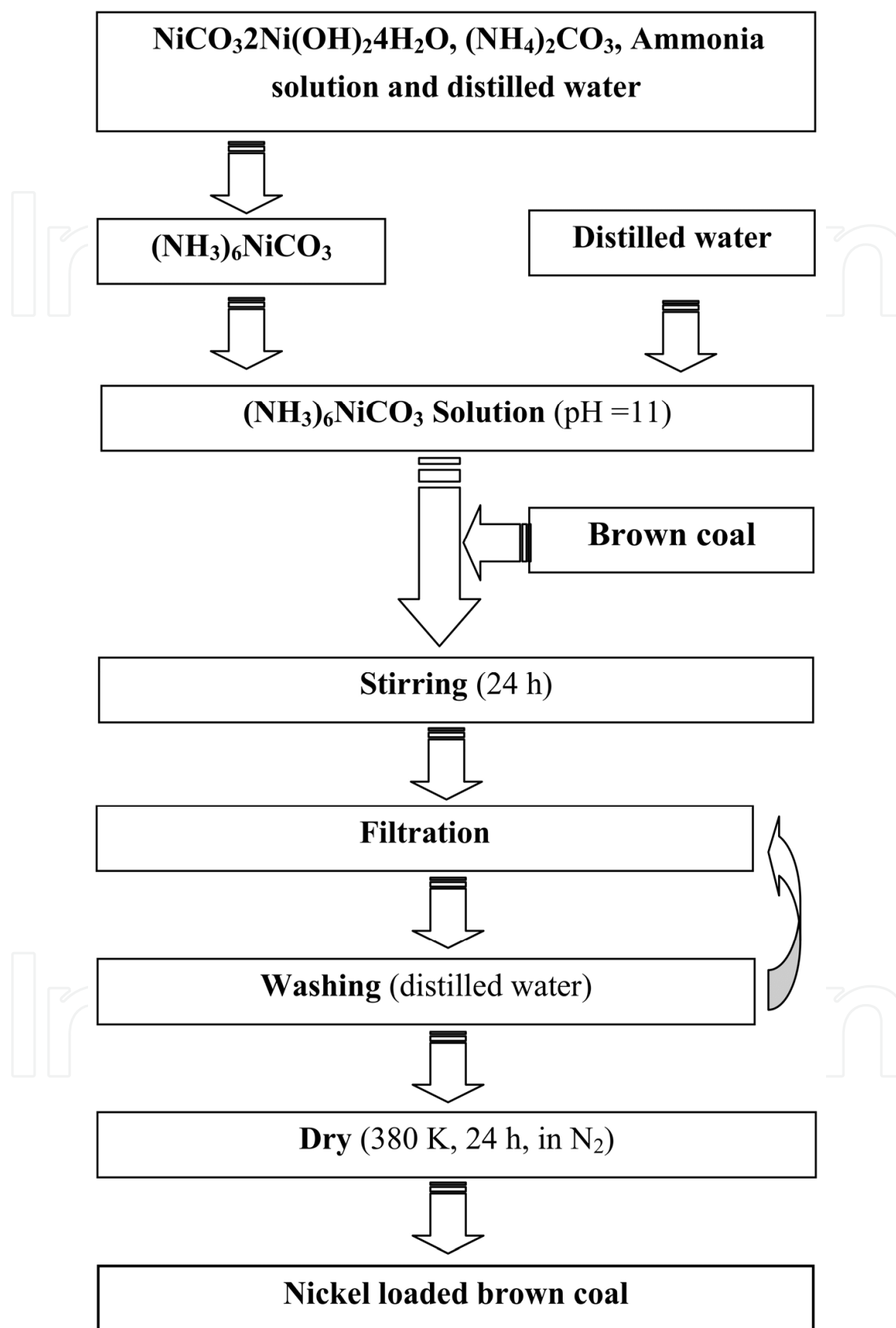
Figure 5. Schematic flow diagram of nickel and brown coal ion–exchange procedure

Figure 6. schematic diagram of nickel loaded brown coal char with structure unit of Ni/BCC.

2.2. Ni/Al$_2$O$_3$ catalyst

A conventional nickel catalyst (No.C13–4, Ni 20±2 wt % SÜD–CHEMIE CATALYSTS JAPAN, Inc.) that was supported with alumina was also used to compare with Ni/BCC catalyst. It was crushed and sieved to the fraction of 0.5 – 1 mm.

3. Catalytic decomposition of tar from woody biomass pyrolysis

Pyrolysis is an important process in energy recovery from biomass and also as a previous stage to other processes such as gasification. Valuable gases, such as H$_2$ and CO, can also be generated by pyrolysis. These gases can be useful, among other applications, in chemical synthesis and high efficiency combustion systems such as fuel cells.

The hydrogen–rich product gas from biomass pyrolysis is believed to become a valuable energy source with natural carbon dioxide. However, biomass has low energy density, so the enhancement of the product gas quality from biomass gasification is necessary. Beside a particular problem which has not been completely solved so far is tar formation. Catalytic processes are considered as the most promising method with the highest potential to contribute a solution to this problem. Temperature is an important variable in thermal decomposition processes of biomass, significantly influencing the product distribution. Pyrolysis is an endothermic process, and the use of low temperatures in this process decreases the input energy for a system that is very positive from an energetic point of view and the system operation is easier than high temperature systems.

For both catalytic activity and economic reason, a nickel catalyst is the most suitable choice and the most widely used in the industry among metals like Co, Pt, Ru and Rh, which were investigated by many authors [10,17–23]. Moreover, nickel based catalysts are reported to be quite effective not only for tar reduction, but also for decreasing the amount of nitrogenous compounds such as ammonia [24]. In most reports, conventional nickel catalysts, which had been developed for steam tar reforming, were tested [6,9,13,15,25,26]. However, the investigations are still limited because of coking [19,22] or the use of expensive materials as catalyst supports (CeO$_2$, Al$_2$O$_3$, Al, SiO$_2$, TiO$_2$, ZrO$_2$, MgO or WO$_3$). Among the above investigations, the most interesting one concerning the current study is brown coal gasification by the addition of a nickel catalyst in fluidized bed gasification at low temperature [21–23]. However, nickel catalyst has only been used for coal gasification itself.

To satisfy both high quality of product gas and use of a cheaper catalyst support (brown coal char), in this study, nickel loaded brown coal char catalyst has been developed for the new purpose of decomposing tarry material from woody biomass pyrolysis. A suitable temperature for catalytic tar decomposition was investigated in a two–stage fixed bed reactor. The effect of temperature on gas yield and carbon conversion have been discussed in detail and compared in the case of non catalyst and Ni/BCC catalyst. The better temperature is a reference result, being used in fluidized bed gasification which is available for continuous tests to assess durability. Catalytic activity was tested, evaluated by woody biomass pyrolysis in a fluidized bed gasifier for both of Ni/BCC and reference catalyst

Ni/Al_2O_3. In a lab scale fluidized bed gasifier (FBG) Experiments, inside of FBG reactor is constructed by two beds, the primary one is a fluidized bed with sand where biomass was fed to produce tar, and the other is a catalyst bed that is used to evaluate and to compare catalytic activity between the new catalyst and a conventional Ni/Al_2O_3 catalyst. The Ni/BCC catalyst is prepared by ion exchange method, dried at 380 K in nitrogen for 24 h, and is then calcined at 923 K in nitrogen for 90 min. Sample for characterization of catalyst was prepared on the fixed–bed reactor under various conditions such as nickel loaded brown coal particle size range of 0.5 to 2 mm, pyrolysis temperature range of 823 to 1023 K that are needed to investigate the effect both of catalyst particle size and pyrolysis temperature on crystallite size of Ni/BCC. The temperature as a function of gas yield and stable activity of catalyst absence of steam are investigated in this chapter.

3.1. Experimental facilities

The two–stage fixed–bed quartz reactor
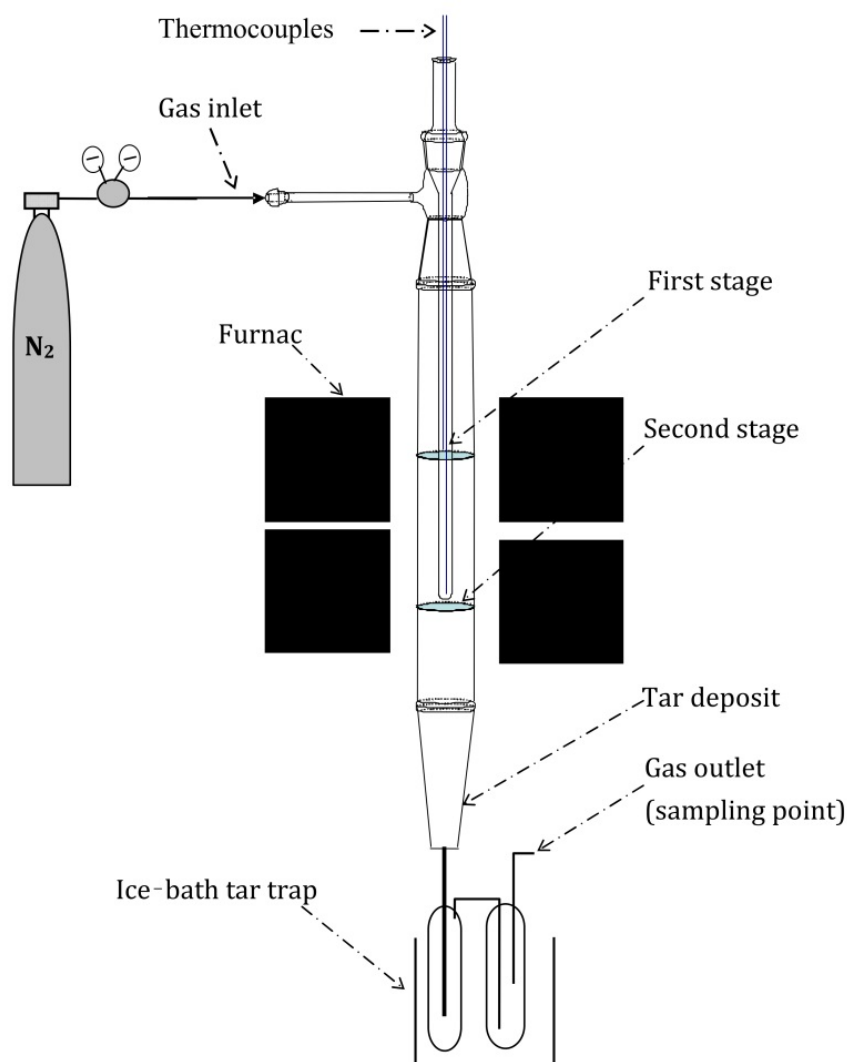
Figure 7. Schematic flow diagram of the two‑stage fixed‑bed quartz reactor

The fluidized bed gasifier
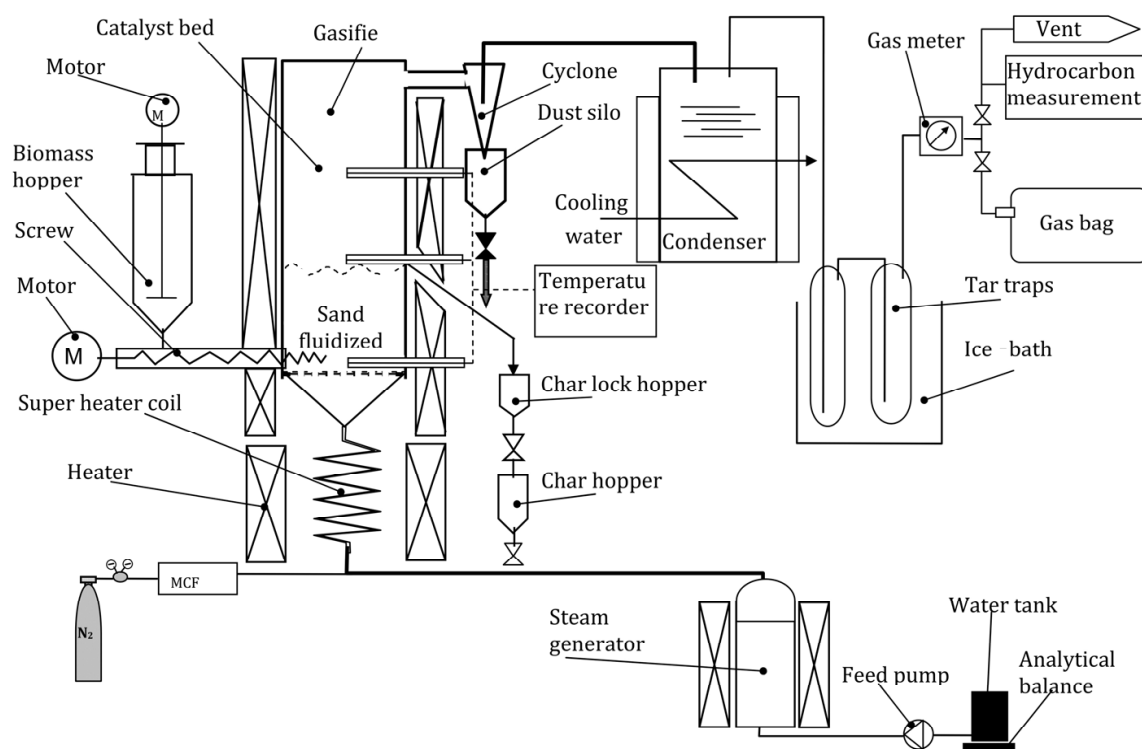
Figure 8. Schematic flow diagram of fluidized bed gasifier

3.2. Results and discussion

3.2.1. Catalyst Evaluation in a Two–stage Fixed–bed Reactor

Figure 9 illustrates the gas yield and the biomass carbon balance of woody red pine pyrolysis in a two fixed–bed quartz reactor. In the case Ni/BCC catalyst, total gas yield increased drastically at a catalyst bed temperature of 923 K, at which the yield of CO and H_2 achieved was 21.2 and 29.5 [mmol/g–sample daf], respectively, approximately three and six times in comparison to sand (Figure 9(a)). It was considered that tarry material was efficiently decomposed by the Ni/BCC catalyst. If we consider the effect of catalytic pyrolysis temperature on gas yield, Figure 9 (a) also shows that the gas yield increased by increasing temperature from 823 to 923 K, thus suggesting tar decomposition can be controlled by chemical kinetics.

Although there was no direct measurement of tar, we have the biomass carbon balance, which is illustrated in Figure 9(b). Among total carbon in biomass, percentages of carbon in product gas (C_ gas) and carbon in char (C_char) could be obtained by analyzing product gas and product char, respectively. Carbon in tar (C_tar) was estimated fairly by a different method: C_tar = 100 – (C_ gas + C_char). In the case of Ni/BCC, we could assume that the total carbon of product gas was released from biomass pyrolysis because the pyrolysis time
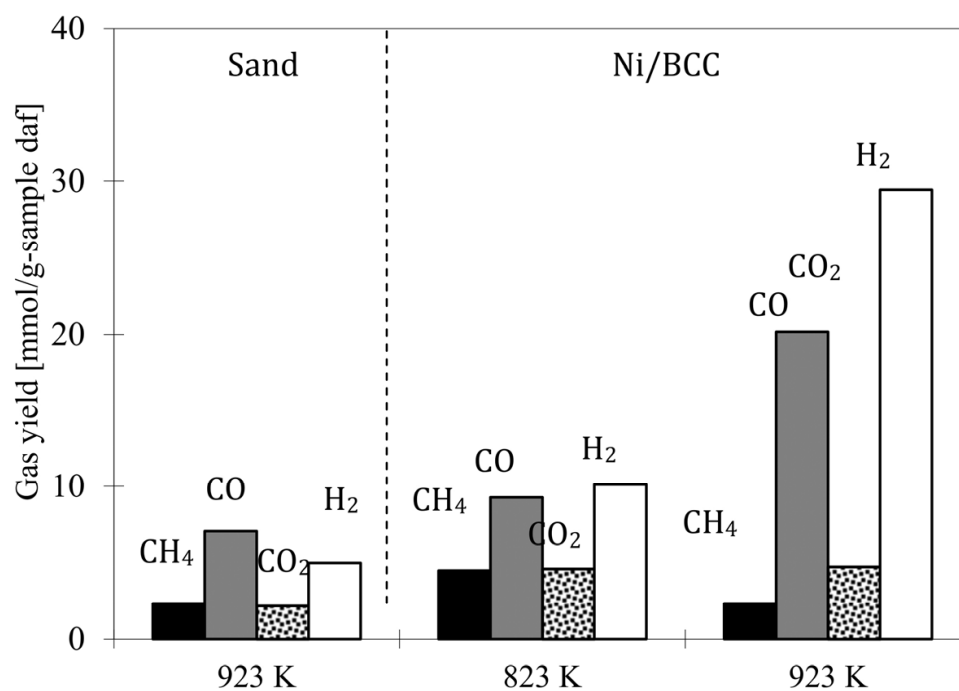
(a)
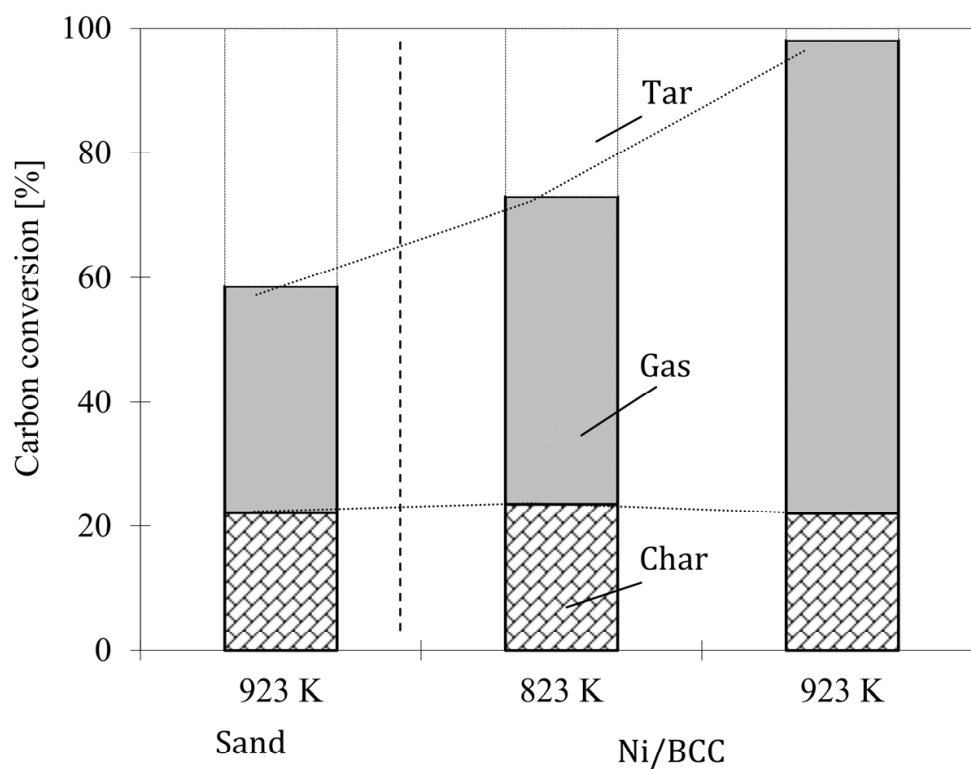
(b)

Figure 9. Effect of temperature on catalyst pyrolysis: (a) gas yields and (b) biomass carbon balance (space velocity 3000)

of 90 min was enough to release most releasable carbon in Ni/BCC at 923 K. The amount of C_chars was almost constant in all cases, because the char is accumulated in the first bed without contacting the catalyst particles at the same temperature of 1173 K. In the case of catalytic tar decomposition, the amount of C_gas increased drastically compared to no catalyst at 923 K. That is to say, the tar was decomposed over Ni/BCC catalyst by Equation, Tar $\rightarrow CO + H_2 + CO_2 + CH_4 + C_2H_4 +$ other hydrocarbon.

When using Ni/BCC catalyst, C_tar approaches zero at 923 K. Moreover, we did not observe tar adhered on the reactor. Thus, it suggests almost all of the tar was decomposed at 923 K under the pyrolysis experimental conditions.

3.2.2. Catalyst Evaluation in a Fluidized Bed Gasifer

In the catalytic activity tests, the formation of products were observed for 60 min, and significant heavy tar was not observed on the pipeline and tar traps. All experiments were performed at 923 K under nitrogen carry gas, space velocity 11000. All calculated results of gas yield and C_gas were the average of specific results from various specific sampling times, which started at 10 min after feeding biomass and then in 20 min intervals. The effects of the catalyst on gas yields (CH_4, CO, CO_2, H_2 yield) are illustrated in Figure 10 (a). The bars from left to right show the results for non–catalyst, Ni/Al$_2$O$_3$ and Ni/BCC catalyst. Using Ni/BCC catalyst, CH_4, CO, CO_2 and H_2 yields were almost the same as those of Ni/Al$_2$O$_3$: 2.8, 15.6, 6.3, 23.1 [mmol/g–sample daf], respectively. Especially, both CO and CO_2 yields increased drastically by 2 times and H_2 by approximately 5 times compared to those of non–catalyst. This result indicates that Ni catalysts are quite effective to decompose tar to useful gases such as CO and hydrogen.

Biomass carbon balance is illustrated in Figure 10 (b). A detailed carbon balance could not be carried out because of difficulty in accurately estimating the tar yield. In a similar way as described above section, we defined C_gas, C_char, C_coke (Deposited carbon on the catalyst) and calculated C_tar:

$$C\_tar = 100 - (C\_gas + C\_char + C\_coke.$$

In the case of no catalyst, C_coke was not observed at all, because coke is assigned to the carbon deposited on the catalyst surface. For the case Ni/BCC catalyst, C_coke was estimated by the difference of carbon in fresh Ni/BCC and carbon in used Ni/BCC catalyst. The amount of C_char was almost constant in all of the cases. This is because the char is accumulated in the fluidized bed without contacting the catalyst particles. In the case of catalytic tar decomposition, the amount of C_gas increased drastically compared to no catalyst. The blank on the top of each bar in Figure 10(b) can be considered as a percentage of C_tar. For Ni/BCC and Ni/Al$_2$O$_3$ catalysts, C_tar was 12.3 and 8.9% and C_gas was 54.9 and 55.1%, respectively. The results show that the Ni/BCC catalyst could not perform as well as the Ni/Al$_2$O$_3$ catalyst to decompose tar under pyrolysis process. This result might be affected by a part of the deposited carbon being on some of the reactive surface of the Ni catalyst, while the raw Ni/BCC catalyst was calcined due to volatile release from the brown coal. However, the results show that both catalysts are quite active to decompose tar.
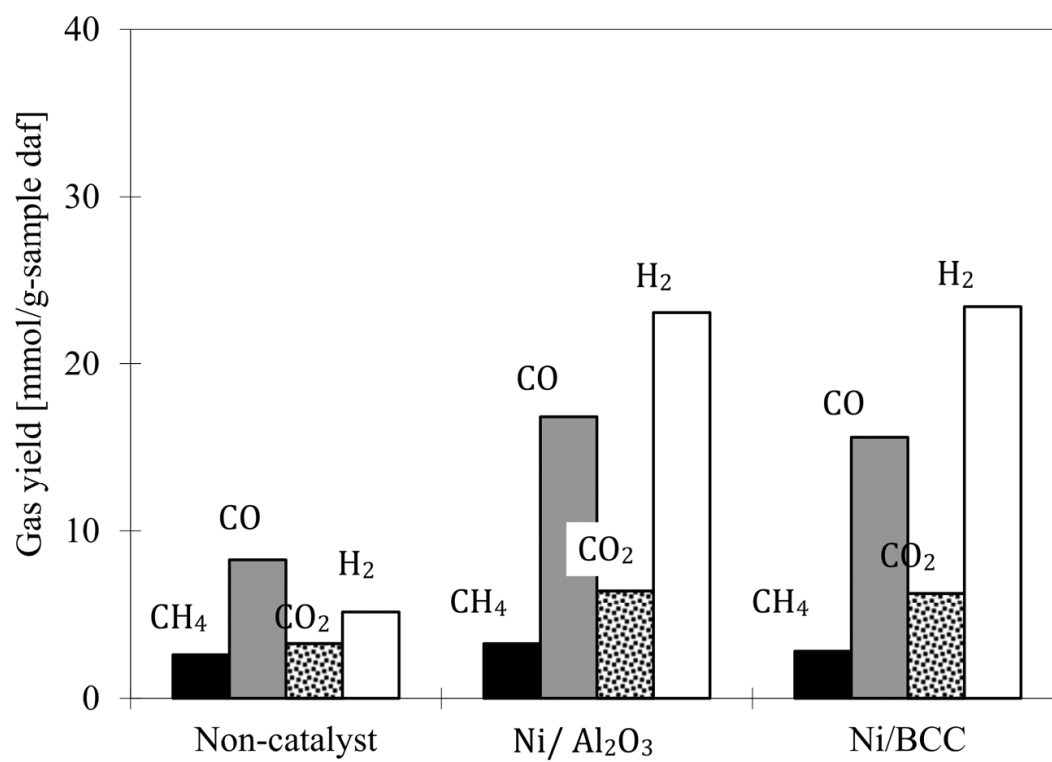
(a)
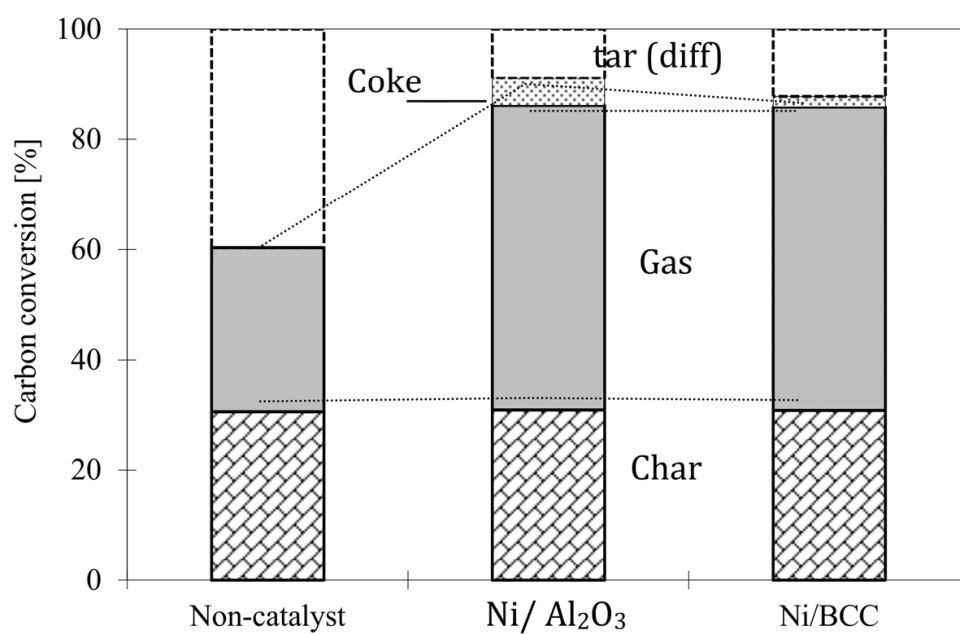
(b)

Figure 10. Comparison of different catalysts and non–catalyst without steam: (a) gas yields and (b) biomass carbon balance at 923 K and no steam (923 K, sv = 11000)

4. Catalytic steam reforming tar from woody biomass gasification

The aim of current study is to increase the coking resistance ability as well as steam gasification of deposited carbon on Ni/BCC catalyst. It was available to regenerate activity of catalyst. By the way, product gases propose to achieve an enhancement of the product gas quality by not only recovering energy from tar reforming but also addition by–product gas from steam gasification of the Ni/BCC char at relative low temperature. To decompose tar of biomass gasification by the use of Ni/BCC catalyst has been investigated under mild conditions in a laboratory scale fluidized bed gasifier with introducing steam as a gasifying agent and nitrogen as the product gas carrier. A conventional Ni/Al$_2$O$_3$ catalyst also was selected to compare with the Ni/BCC catalyst in the presence of steam. In this study, the Ni/BCC catalyst was consumed at different steam feed rate so as determine the effect of steam feed rate on the crystallite size of catalyst; catalytic tar reforming temperature, the space velocity as a function of the gas yield and biomass carbon conversions in fluidized bed gasifier were investigated. The product gas components was discussed in detail and compared between both cases of the absent of steam and the presence of steam.

4.1. Discussion of catalytic steam tar reforming pathway

Figure 11 shows simple pathway of the woody biomass gasification process with Ni/BCC catalyst. The woody biomass was first pyrolysis to form gas, tar and char at 923 K. Both useful gas and tar passed through the catalyst particles. Tar was dissociatively adsorbed onto a nickel site where nickel catalyzed dehydrogenation occurs. With steam injection tar would be cracked and reformed follow the mechanism.
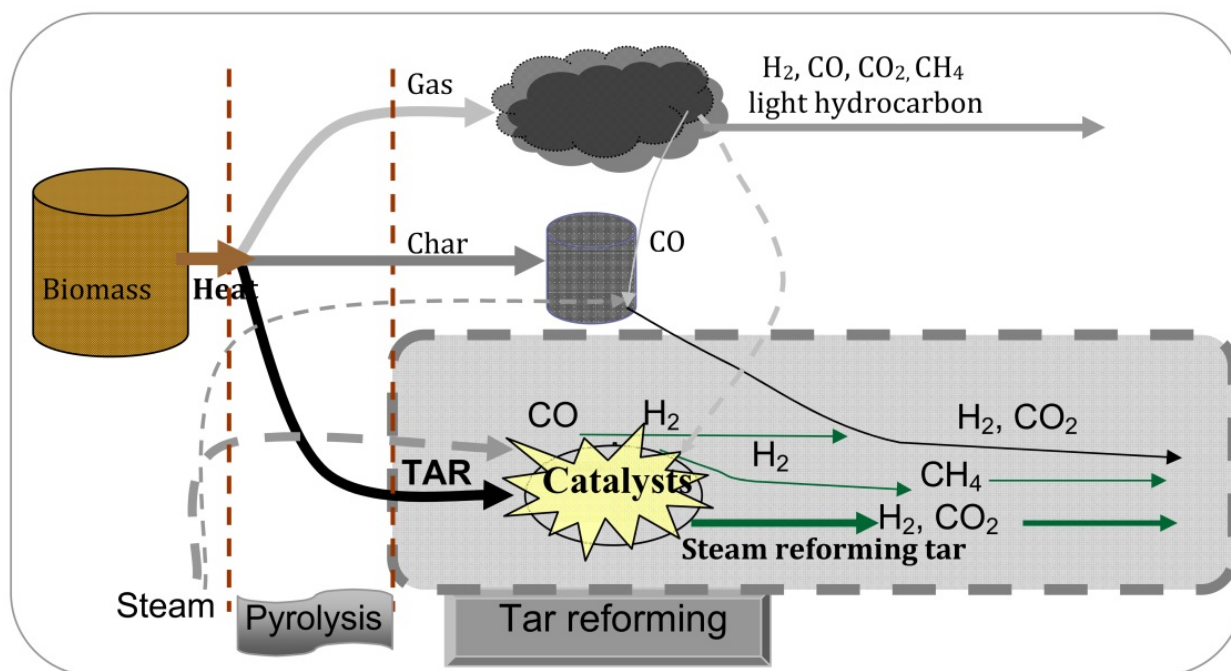
Figure 11. Schematic pathway of biomass pyrolysis and tar reforming using Ni/BCC catalyst

The chemistry of coal (biomass) gasification is usually depicted to involve the following reactions of carbon and steam [29]. The standard enthalpy change (gram molecules) at 298 K is shown for each reaction. The most important reactions are listed in Table 1[29–31]

Process	ΔH_{298}^{O} (kJ/mol)	
Steam reforming		
$CH_4 + H_2O = CO + 3H_2$	+ 206	(7-1)
$C_nH_m + nH_2O = nCO + n + (m/2)H_2$	+ 1175[a]	(7-2)
CO_2 reforming		
$CH_4 + CO_2 = 2CO + 2H_2$	+ 247	(7-3)
Gasification		
$C + H_2O \rightarrow CO + H_2$	+ 131.3	(7-4)
$C + 2H_2O \rightarrow CO_2 + H_2$	+ 90.2	(7-5)
$C + CO_2 \rightarrow 2CO$	+ 172.4	(7-6)
Water–gas shift reaction		
$CO + H_2O \rightarrow CO_2 + H_2$	- 41.1	(7-7)
Methanation		
$2CO + 2H_2 \rightarrow CH_4 + CO_2$	- 247.3	(7-8)
$CO + 3H_2 \rightarrow CH_4 + H_2O$	- 206.1	(7-9)
$CO_2 + 4H_2 \rightarrow CH_4 + H_2O$	- 165.0	(7-10)
$C + 2H_2 \rightarrow CH_4$	- 74.8	(7-11)

a for nC_7H_{16}

Table 1. Synthesis gas reactions

4.2. Catalyst evaluation in steam gasification process in fluidized bed gasification

The conventional Ni/Al_2O_3 catalyst and Ni/BCC catalyst available for steam reforming were used to test tar reforming performance. As mentioned in section 7.1 and discussed in section 7.3, the deposited carbon may cause for deactivating catalysts due to covering activate site of catalysts. In this section, all experiments were performed under steam injection with s/c: 0.6 mol/mol. The added steam was expected to suppress the deposited carbon on activate surface of catalysts. In this section, the effect of steam addition on tar conversion, gas yields, and carbon conversion were investigated. The reactivity both of the Ni/BCC and Ni/Al_2O_3 have been compared and discussed in detail.

In the activity tests, the formation of products were observed for 120 min, all calculated results of the gas yields and C_gas were the average of the specific results from various

specific sampling times, which started at 20 min after feeding biomass and then in 20 min intervals.

As illustrated in Figure 12 (a), the gas yields are shown lowest for non–catalyst, while higher gas yields have achieved for the catalysts. The great improvement of product gas for the case of Ni/BCC catalyst should be given more attention. Most main gas components (CH_4, CO, CO_2, H_2) were higher than those of Ni/Al_2O_3 catalyst. Especially, in the case of the Ni/BCC catalyst, CO and H_2 yield were 10.8 and 12.3 [mmol/ g–sample daf] higher than those of the Ni/Al_2O_3 catalyst. These satisfactory results could be explained by a part of the deposited carbon on the Ni/BCC catalyst and Ni/ BCC char had been gasified in the presence of steam according to the reaction pathway as following reaction equations (Eqs. (7-4), (7-5), and (7-6)) in the Table 1.

Steam might also produce a larger active surface of Ni/BCC by steam gasification of deposited carbon on the surface of catalyst, which is also evidenced by BET data of used catalyst. After 1 h operation, total free surface of the Ni/Al_2O_3 decreased from 104 to 32 m^2/g due to reduction of nanopores by blockage of deposited carbon and catalyst particle growth. While, total free surface of Ni/BCC lightly reduced from 350 to 339 m^2/g, this is due to characteristic porosity of brown coal char. The results indicate that steam plays a very important factor to regenerate activity of the new catalyst by steam gasification of deposited carbon on catalyst and to significantly enhance the quality of product gas of woody biomass gasification.

Biomass carbon balance is illustrated in Figure 12 (b). It was carried out in a similar way as described in section 7.3 The blank on the top of each bar can be considered as a percentage of the C_tar which was calculated by equation 3-5 in section 7.3.

It is different from the pyrolysis process, approximately 16.5% carbon in the fresh Ni/BCC catalyst was gasified in the presence of steam. Its percentage was defined by comparing between carbon in the fresh Ni/BCC catalyst and carbon in used Ni/BCC catalyst. In the presence of the Ni/BCC, biomass carbon conversion (C_gas) was calculated by subtraction between carbon of total product gas and conversion carbon of fresh Ni/BCC, which is mentioned on above. Using that method, we found that highest C_gas and lowest C_tar were achieved as 66 and 4.4% for Ni/BCC catalyst test, respectively, while the C_gas and C_tar obtained were only 59.9% and 7.4% for Ni/Al_2O_3 catalyst test, respectively. Biomass tar conversion obtained was approximately 88.9% in Ni/BCC catalyst. The results indicate better catalyst activity for Ni/BCC. The detailed mechanism for this high activity is unclear at the present, however, it can be explained that some of the following characteristics of the Ni/BCC catalyst might be associated with this activity: well distribution of nickel particles due to carbon functional group in brown coal, high porosity of the catalyst, mineral component. In addition, Tomita *et al.* [32] reported that in the presence of steam, tar might be absorbed on catalyst and then be gasified without forming soot. Even if carbon was formed on the catalyst surface, it could be easily gasified. He also found that the carbon deposited over nickel was rapidly gasified with hydrogen at 873 K by reaction 7-11 in Table 1 [33]. This fact that can be observed both of CH_4 and H_2 yields are higher than that of the Ni/A_2O_3 catalyst.
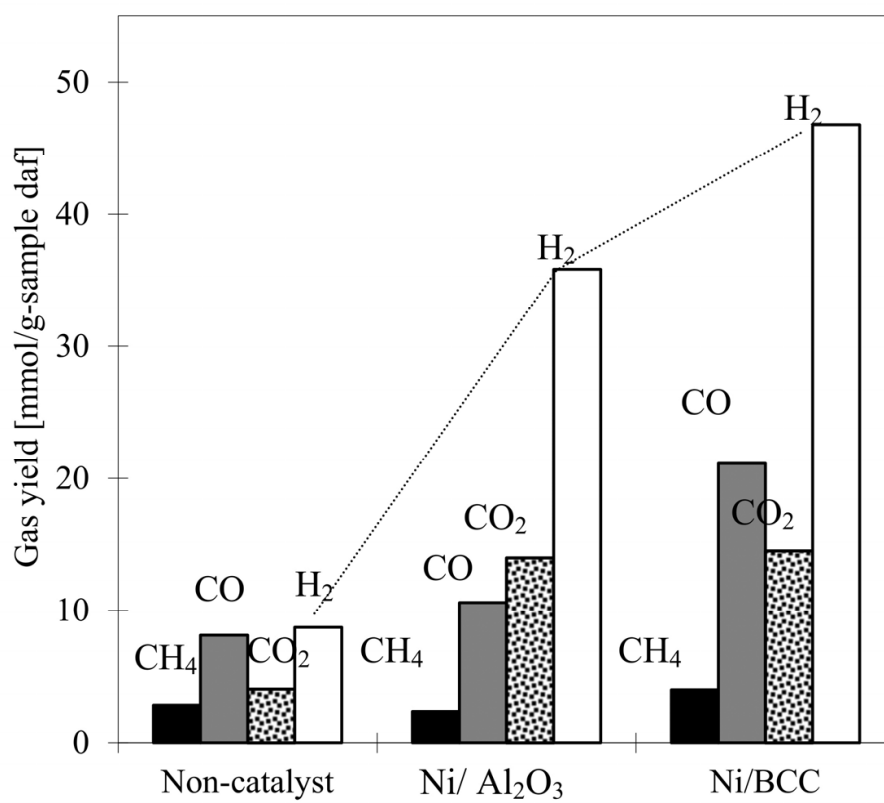
(a)
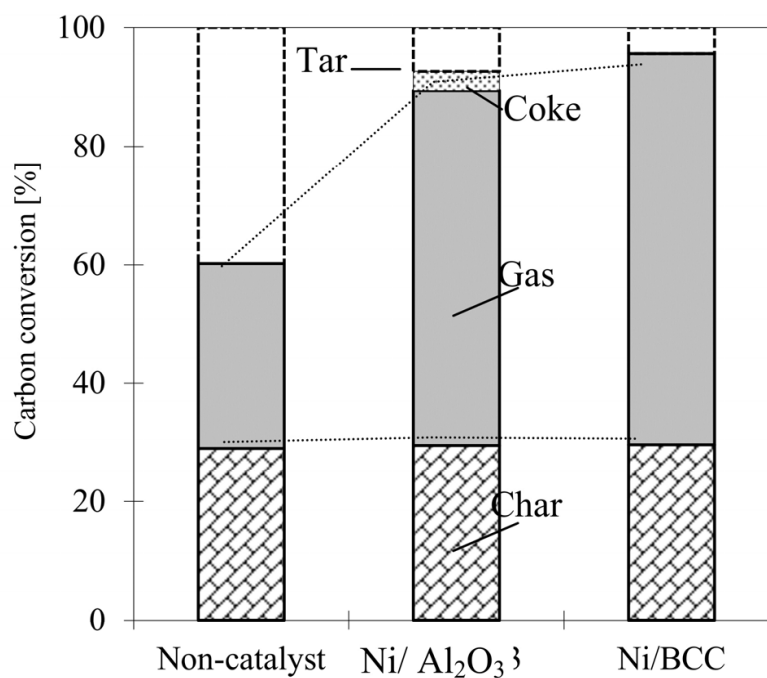
(b)

Figure 12. Comparison of different catalysts and non–catalyst in the presence of steam: (a) gas yields and (b) biomass carbon balance (923 K, sv = 10000, s/c =0.6)

5. Summary and conclusions

Nickel loaded brown coal char acts a new catalyst for decomposing tar of woody biomass gasification in a two-stage fixed-bed and fluidized bed gasifier has been investigated. With the advantages of catalytic steam tar reforming is carry out at low temperature. On the other hand, catalytic reforming tar methods have significant possibilities in low temperature gasification processing for high product gas quality. This chapter attempts to a comprehensive knowledge for low temperature pyrolysis and gasification process covering study of operation conditions affecting catalytic activity behaviors of nickel loaded brown coal char catalyst.

For the effect of pyrolysis temperature on the crystalline size of nickel particle size, it is slightly affected by temperature lower than 923 K, but great affected by temperature higher than 973 K.

Two-stage Fixed-bed Reactor has been identified as processing the good activity even at low temperature 923 K.

The Ni/BCC catalyst could not perform as well as the Ni/Al$_2$O$_3$ catalyst to decompose tar under pyrolysis process. However, the results show that both catalysts are good active to decompose tar from biomass pyrolysis at 923 K.

The experimental results show a new catalyst having good catalytic activity and stability in the presence of steam at 923 K.

In the new catalyst application with the presence of steam, Ni/BCC catalyst exhibited more activate than conventional catalyst Ni/Al$_2$O$_3$.

It was found that, catalyst has a good performance and stability at 923 K. Approximately 89.5 % of biomass tar was reformed to useful gas components (CO, H$_2$, CH$_4$).

Steam has already proved to be very important in activating the new catalyst and significantly enhances the quality of product gas of woody biomass gasification with high hydrogen concentration of product gas.

The results suggest that the Ni/BCC catalyst offers a potential to be used as a tar steam reforming catalyst in biomass gasification.

Author details

Le Duc Dung
School of Heat Engineering and Refrigeration, Hanoi University of Science and Technology, Vietnam

Le Duc Dung, Kayoko Morishita and Takayuki Takarada
Department of Chemical and Environmental Engineering, Gunma University Faculty of Engineering, Japan

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