Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/petroleum-coal
Petroleum & Coal 57(3) 216-224, 2015

HYDROGEN RICH GAS PRODUCTION VIA STEAM GASIFICATION OF BAGASSE OVER BIMETALLIC Ni-Fe/γ-Al_2O_3 NANO-CATALYSTS

Sajedeh Jafarian[1], Ahmad Tavasoli[1], Ali Karimi[2]

[1]School of Chemistry, College of Science, University of Tehran, Tehran, Iran
[2]Gas Division, Research Institute of Petroleum Industry, Tehran, Iran

Received March 9, 2015, Accepted June 2, 2015

Abstract
Biomass gasification in the presence of steam is a promising method for production of hydrogen. In this research, 12%Ni-6%Fe/γ-Al_2O_3 nanocatalysts were prepared and characterized by ICP, BET, XRD, TPR, H_2 chemisorption, and TEM techniques. Nano-catalysts were assessed in a batch micro-reactor at 850°C, 1 atm pressure and in the presence of steam (0.6 ml/min). Comparing with pyrolysis, using steam for non-catalytic gasification of bagasse increased the hydrogen yield (mmol/g bagasse) by a factor of 3 and the selectivity of H_2 on the produced gas from 34.9 to 48.6%. In addition, gasification in the presence of Ni-Fe/γ-Al_2O_3 nanocatalyst prepared by microemulsion technique increased the hydrogen yield by factor of 2.37 and decreased the methane yield by factor of 0.51.

Keywords: Biomass gasification; steam reforming; microemulsion technique; hydrogen yield; 12%Ni-6%Fe/γ-Al_2O_3 nanocatalysts.

1. Introduction

The oil price is rising due to declining in fossil fuel resources. Excessive consumption of energy and international events as well as environmental consideration especially about greenhouse gases emission problems, make finding new fuel processes and resources indispensable. Hydrogen as an emerging energy carrier creates a promising future for development of a clean and accessible source of energy [1-3]. It can be also a kind of renewable fuel because it can obtain from catalytic biomass processing [4]. Gasification is a process in which solid or liquid carbonaceous materials, such as biomass, react with air, oxygen, or steam to produce a gas containing CO, H_2, CO_2 and CH_4 in various proportions [5-6]. Different biomass gasification methods such as pyrolysis, supercritical water gasification and gasification via biomass steam reforming have been investigated to produce hydrogen rich gas [7]. Because of higher hydrogen yield and lower tar and char production, biomass gasification with steam reforming compared to pyrolysis, and milder reaction conditions compared to supercritical water gasification, can be a good candidate for hydrogen production [8].

Biomass gasification with any thermo chemical processes results in a high proportion of gaseous products (i.e. carbon dioxide, water, carbon monoxide, hydrogen and light hydrocarbons) as well as small quantities of char and tar [9-10]. Producing char and tar causes series of problems such as clogging and condensation followed by lines and filters blocking on downstream equipment [11-12]. Steam reforming has high ability to crack tar, so it is the most attractive reaction that occurs through biomass gasification process, especially in catalytic systems. Over the catalyst, tar converts to synthesis gas and causes gas yield increasing. Also, catalysts have been applied to decrease the coke formation in this kind of biomass hydrothermal process [13].

Three types of catalysts have been studied, developed and used in biomass gasification via steam reforming. They are classified as natural mineral, alkali metal and transition metal catalysts [14-15]. Dolomite and olivine have been considered as effective natural mineral catalysts for biomass tar reforming and cracking. They are inexpensive, readily available and good tar reforming [16-17]. Alkali metals such as lithium, sodium, potassium and rubidium provide a considerable increase in initial reaction activity, but particle agglomeration at higher temperatures decreases metal catalytic performance [15].

Transition metal based catalysts, particularly supported Ni catalysts, have been widely employed for biomass gasification due to their high activity in tar cracking and improving the quality of the produced gas [18]. However, these catalysts suffer rapid deactivation as a result of coke deposition, sintering of metal particles and carbon fouling at high temperatures [19].Essential factors that describe the high catalytic activity of the nickel based catalysts are small crystallite size and high degree of dispersion of nickel on the supports [20].

Also, iron based and promoted catalysts are attractive for researchers in gasification fields of study. The Fe modified Co catalysts have been applied widely for the steam reforming of oxygenates. It has been reported that Fe enhances the catalyst activity for breaking C–C and C–H bonds and increases carbon deposition and producing H_2 yield. Moreover, because of high oxygen affinity, Fe can increase the catalyst coverage with oxygen atoms during the steam reforming reactions. The property makes iron a good choice for catalytic reforming of oxygenates [21-33].

The nature of support and addition of promoters also play important roles in defining the activity and service life of the catalyst. Catalyst with high surface area of support generally causes higher catalytic activity. Comparative studies have shown better performance for inhibiting carbon fouling on basic supports such as MgO and La_2O_3 [26-33]. However, alumina is more interesting due to its industrial use. The high surface area of γ-Al_2O_3 provides higher metal dispersion while α-Al_2O_3 shows better mechanical and thermal resistances.

In our previous work [30] we studied bagasse conversion to hydrogen rich gas via pyrolysis. In this research, to increase in hydrogen yield, bagasse was used as biomass feedstock for catalytic steam-gasification in the presence of steam. Ni-Fe/γ-Al_2O_3 bimetallic nanocatalysts were prepared with different particle sizes. The performance of bagasse gasification via steam reforming process in presence of steam and prepared catalysts was compared with non-catalytic and catalytic pyrolysis in the absence of steam.

2. Experimental

2.1 Materials

The bagasse biomass as feedstock was supplied from Haft-Tappe Industries. The material was washed, dried, grinded and sieved to achieve particle sizes up to 1 mm. The CHNS analyses of used bagasse were C=58.1%, O=34.57%, H=6.45%, N=0.69% and S=0.19%.

2.2 Catalyst preparation

The bimetallic Ni-Fe nano catalysts supported on γ-Al_2O_3 were prepared by impregnation and reverse microemulsion techniques. For all the catalysts, the weight percentage of loaded Ni and Fe were adjusted at 12 and 6, respectively. The details of preparation, drying and calcinations methods of the nano catalysts were carefully described on our previous work [30]. Table 1 shows the composition and preparation details of the calcined catalysts [30].

Table 1 Chemical composition, preparation details and physico-chemical properties of the calcined catalysts.

Sample	Preparation route	W/S ratio	BET surface area (m^2/g)	Percentage Reduction	Percentage Dispersion	dp (nm) determined by XRD	dp (nm) determined by TEM
support	-		212.4	-	-	-	-
C_1	Impregnation	-	145.3	32.2	10.1	18.8	21.17
C_2	Microemulsion	0.83	173.3	39.9	12.1	15.1	15.7
C_3	Microemulsion	0.5	181.6	49.1	23.5	7.2	7.8
C_4	Microemulsion	0.16	190.1	60.4	43.4	3.7	4.1

2.3 Catalyst characterization

Nano catalysts were characterized by ICP, BET, XRD, TPR, H_2 chemisorption, and TEM techniques. The details of characterization and calculation methods of the physico-chemical properties of the nano catalysts were carefully described on our previous work [30].

2.4 Reaction setup

Figure 1 shows the reaction setup for tests. As shown, the reaction was performed in a fixed bed reactor made of a quartz glass tube with 800 mm long and 10 mm internal diameter.

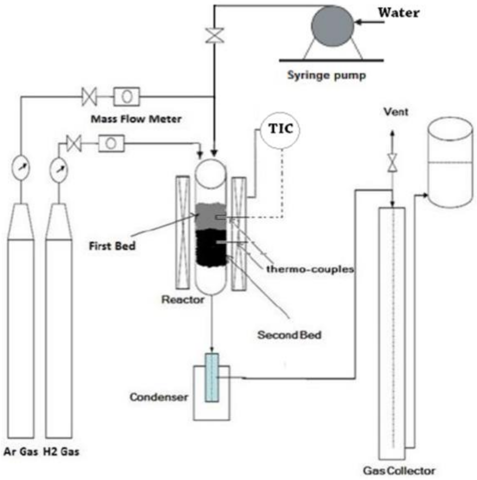

Figure 1 Experimental setup

The experiments were divided to two general series of catalytic and non-catalytic processes. Catalyst bed was fixed in center of the reactor. The reactor was located inside a tubular furnace with 20mm ID and 200mm OD with total heating length of 700mm. Furnace temperature was controlled using a PID temperature controller and measured using a K-type thermocouple. Argon was used as inert carrier gas with exactly 30ml/min flow rate using mass flow controller. Water was injected to the reactor using a syringe pump with desired flow rate. Reaction time, temperature and water flow rate were 30 min, 850°C and 0.6ml/min, respectively. The gas leaving the reactor was condensed and separated into liquid and gaseous fractions. The liquid fraction was collected in a liquid trap of ice-salt bath and the gaseous fraction was collected over a sodium chloride saturated brine solution in a graduated column. The volume of collected gases was measured from displacement of the solution in column. Before bagasse loading, the catalysts were reduced by hydrogen with 30ml/min flow rate at 450^{O}C for 2h. The reactor was allowed to cool down at the end of each experiment. The quality and quantity of produced gaseous mixture were analyzed using gas chromatography technique (Varian 3400 and Teyfgostar-Compact). The condensed tar in glass condenser and char left inside the reactor were measured by taking the difference in weights of glass condenser and reactor before and after the reaction. All experiments were repeated twice under the same experimental conditions and the data reported herein are averages of repetitive runs.

3. Results and discussion

3.1 Catalysts characterization

The physico-chemical properties of the prepared catalysts extensively described on our previous work [30]. A brief report of these results is shown on Table 1. Results of surface area measurements on this table shows that incorporation of Ni (12 wt%) and Fe (6 wt%) reduces surface area. This may indicate partially blocking of the support pores after incorporation of the metals. Furthermore, the catalyst prepared by the microemulsion method and with minimum water to surfactant ration (C_4) has the highest S_{BET} and as a result lowest pore blockage. The TEM micrographs of the prepared catalysts were shown on our previous work [30]. According to these micrographs the average particle size for the C_1-C_4 catalysts are 21.7, 15.7, 7.8 and 4.1 nm, respectively (Table 1). Also, percentage dispersion calculated from H_2 chemisorption tests, which are shown on Table 1, display considerable increase (from 10.1 to 40. 34%) when microemulsion method was used for catalyst preparation. These results are in agreement with the TEM consequences. X-ray diffraction (XRD) experiments of the calcined catalysts [30] showed tetragonal Ni-Fe phases, which suggest formation of Ni-Fe alloys with more Fe-rich than the average composition (Fe/Ni = 0.5) [29]. Table 1 also shows the average Ni-Fe sizes for the catalysts calculated from the XRD spectrum and Scherrer formula. Based on XRD, the average particle sizes for the C_1-C_4 catalysts are 18.8, 15.1, 7.2, and 3.7 respectively. The sizes determined by XRD are close to the results obtained by TEM. The results of all characterization tests show that, using microemulsion technique especially at lower water to surfactant ratios considerably decreases the particle sizes and increases the percentage dispersion. Table 1 also shows the percentage reduction for the catalysts that are determined from oxygen titration and temperature programmed reduction tests [30]. As shown, catalysts with lower average particle size and higher dispersion have higher percentage reduction.

3.2 Reaction

In order to determine performance of bagasse gasification in presence of steam, two non-catalytic processes, pyrolysis and steam-gasification, were compared. Thereafter, the effects of catalyst type on the conversion, gasification yield and product gas composition were studied. All experiments were performed at the temperature of 850°C and atmospheric pressure.

3.2.1 Non-catalytic tests

Table 2 presents the non- catalytic pyrolysis and steam-gasification yields (mmol of gas/g of bagasse) for the all gaseous products (H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6) at a reaction time of 30 min, bagasse loading of 1g and water flow rate of 0.6 ml/min.

Table 2 The comparison of non-catalytic pyrolysis and gasification via steam reforming yields (mmol/g bagasse) for the whole gaseous products and H_2,CO,CO_2,CH_4 and heavier hydrocarbons and carbon conversion and LHV (T = 850 °C, reaction time = 30 min, bagasse loading: 1g).

Product	Pyrolysis	Steam reforming
H_2	3	9
CH_4	0.8	0.6
CO_2	0.2	1
CO	3.8	7.5
Heavier hydrocarbon	0.12	0.09
Total gas	8.6	18.5
(%)η_c	10.5	19.77
LHV(KJ/Nm^3)	1248.66	2203.408

It has been referred by different authors that the biomass gasification involves several sequential reactions given below [31].

Reaction	Stoichiometry		Enthalpy (kJ/mol)
Pyrolysis	$C_6H_{10}O_5 \rightarrow 5CO + 5H_2 + C$	(1)	180
	$C_6H_{10}O_5 \rightarrow 5CO + CH_4 + 3H_2$	(2)	300
	$C_6H_{10}O_5 \rightarrow 3CO + CO_2 + 2CH_4 + H_2$	(3)	-142
Partial oxidation	$C_6H_{10}O_5 + 0.5O_2 \rightarrow 6CO + 5H_2$	(4)	71
	$C_6H_{10}O_5 + O_2 \rightarrow 5CO + 5H_2 + CO_2$	(5)	-213
	$C_6H_{10}O_5 + 2O_2 \rightarrow 3CO + 5H_2 + 5H_2$	(6)	-778

Steam reforming	$C_6H_{10}O_5 + H_2O \rightarrow 6CO + 6H_2$ (7)	310
	$C_6H_{10}O_5 + H_2O \rightarrow 4CO + 8H_2 + 2CO_2$ (8)	230
	$C_6H_{10}O_5 + H_2O \rightarrow 6CO_2 + 12H_2$ (9)	64
Water-gas shift	$CO + H_2O \rightarrow CO_2 + H_2$ (10)	-41
Methanation	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$ (11)	-211

The overall chemical conversion can be represented by the below simplified net reaction:

$$Biomass + O_2\ (or\ H_2O) \rightarrow CO, CO_2, CH_4, H_2, H_2O + other\ CHs + tar + char + ash \qquad (12)$$

Moreover, carbon deposition is the important side reaction in gasification of biomass because of the decomposition of organics (Eq. 13), CH_4 (Eq. 14), and disproportion of CO (Eq. 15) and also the reaction of CO or CO_2 with H_2 (Eqs. 13 and 14). Oxidizing compounds such as steam can act as the favorable factors for the elimination of carbon deposit (Eq. 18) [31].

$C_nH_mO_k \rightarrow C_xH_yO_z$ + coke (13)
$CH_4 \rightarrow C + 2H_2$ $\Delta H^o = -74.9$ kJ/mol (14)
$2\ CO \rightarrow C + CO_2$ $\Delta H^o = -172.4$ kJ/mol (15)
$CO + H_2 \rightarrow C + H_2O$ $\Delta H^o = -131.9$ kJ/mol (16)
$CO_2 + 2H_2 \rightarrow 2H_2O + C$ $\Delta H^o = -90.1$ kJ/mol (17)
$C + H_2O \rightarrow CO + H_2$ $\Delta H^o = 131.3$ kJ/mol (18)

Since bagasse biomass composed of cellulose, hemicellulose and lignin, it can be expected that the above reactions also occur for gasification of bagasse, but under the given conditions, partial oxidation reactions due to lack of oxygen occur rarely and steam reforming, water gas shift and methanation were the most important reactions in these processes.

The results on Table 2 indicate that, the final product gas composition of the bagasse gasification process in noncatalytic test is the result of the combination of the above mentioned series of complex and competing reactions.

The presence of steam in the reaction increased the amount of gas generated from 8.6 to 18.5 mmol/g baggase. As shown, H_2, CO and CO_2 yield increased but no significant change in the amount of CH_4 and light hydrocarbons (C_2H_4 and C_2H_6) were observed. The increase in the H_2, CO and CO_2 yield and the decrease in the methane yield can be attributed to the steam reforming and water gas shift processes (Eqs. 7-10). On the other hand, steam reforming reactions are endothermic and gasification occurs at high temperature, therefore these reactions are more likely to occur. As shown in Table 2, the carbon conversion efficiency (η_c) and the dry heating value (LHV) of the product gas in the presence of steam increased. According to Eq. 19, LHV of the product gas is proportional to amounts of CO and H_2 so the presence of steam led to increase the amount of LHV from 1248.66 to 2203.408 (KJ/Nm^3).

$$LHV = (30 \times CO + 25.7 \times H_2 + 85.4 \times CH_4 + 151.3 \times (C_2H_4 + C_2H_6) \times 4.2\ (kJ/Nm^3) \qquad (19)$$

3.2.2 Catalytic tests

Catalytic steam gasification of bagasse was performed in the presence of C_1 (prepared by the impregnation method) and C_2-C_4 (prepared by the microemulsion method) catalysts using 1g bagasse, 0.6 ml/min water flow rate, 30 min reaction time and 850°C reaction temperature. Figure 2 illustrates the total gas yields (mmol of gas/g of bagasse). From this figure, it becomes evident that addition of catalyst increases the gas production by a factor of 1.67–2.21, depending on the catalyst preparation method. Also, this figure represents that the performance of the catalyst prepared with the microemulsion method is noticeably higher than that of the catalyst prepared by impregnation. Furthermore in case of C_2-C_4 catalysts prepared by microemulsion technique, the total gas yield increased to 35.6 - 41 (mmol/g bagasse) compared to C_1 prepared by impregnation method. The data on Table 1 showed that, using microemulsion technique increased the dispersion and percentage reduction of the active metals on the Ni-Fe/γ-Al_2O_3catalyst by 28.2% and 33.3%, respectively compared to C_1 (impregnated catalyst). Moreover, the catalysts made by microemulsion have smaller particle size, less pore blockage, higher S_{BET} and pore volume and higher dispersion (Table 1), led to better stability of the products and the gasification activity.

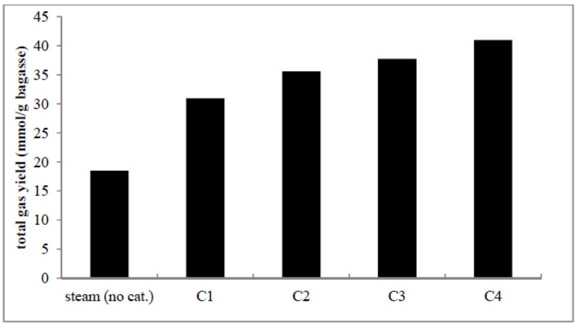

Fig. 2 Total gas yields for non-catalytic and C_1-C_2 catalyzed gasification via steam reforming of bagasse (T: 850°C, reaction time: 30 min)

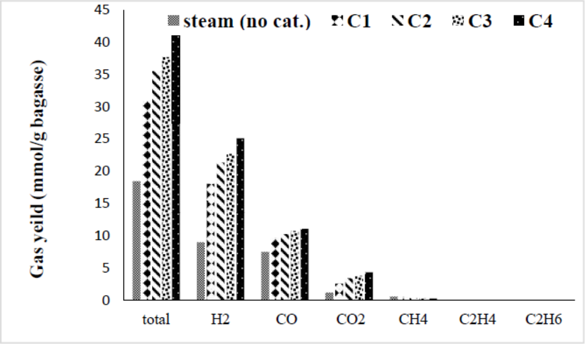

Fig. 3 The bagasse product gasification yields for non-catalytic and C_1-C_4 catalyzed gasification via steam reforming of bagasse (T: 850°C, reaction time: 30 min)

Figure 3 compares the yields of hydrogen, carbon monoxide, carbon dioxide, methane and light gaseous hydrocarbons obtained from noncatalytic and catalytic gasification of bagasse at 850°C, in the presence of C_1-C_4 catalysts. As shown, addition of the C_1 catalyst (prepared by impregnation) increased the hydrogen and carbon monoxide production by a factor of 2 and 1.28 respectively, while the C_2 catalyst (prepared by microemulsion) with the same Ni, Fe loading increased the hydrogen and carbon monoxide production by a factor of 2.37 and 1.37compared to noncatalytic gasification. At the same time, the amount of CO_2 increased to some extent. Furthermore in case of C_2-C_4 catalysts prepared by microemulsion method, C_4 catalyst increased hydrogen and carbon monoxide production compared to noncatalytic gasification by a factor of 2.8 and 1.5 respectively, but the carbon dioxide production rate increased slightly. However, In the presence of a catalyst, production of methane and light hydrocarbons is very low. It is demonstrated that the catalyst with higher Ni-Fe dispersion (catalysts prepared with microemulsion method) is more active for cleaving C-O bonds compared to C_1 (catalysts prepared by impregnation method), so that the carbon conversion efficiency (η_c) increased to maximum value 33% (Figure 4).

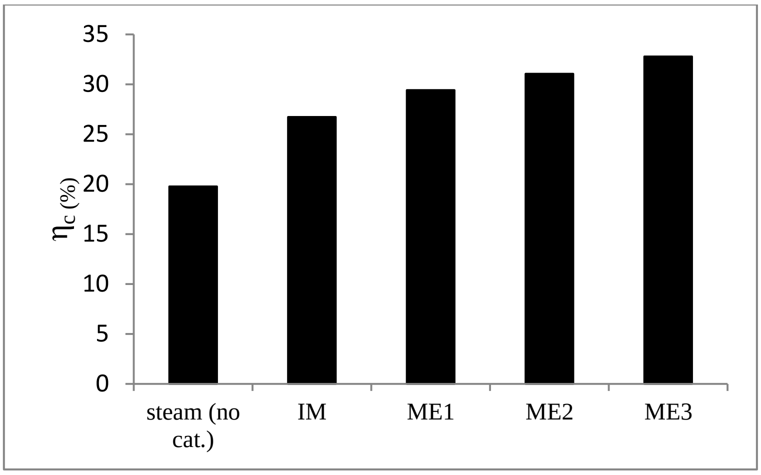

Figure 4 Comparison of carbon conversion amounts between non-catalytic and catalytic gasification via steam reforming

Higher dispersion of Ni and Fe in the case of the catalysts prepared with the microemulsion technique enhances the cracking and reforming of tar compounds with steam which in turn lead to high increase in the hydrogen production. Moreover, high oxygen affinity of Fe can increase the catalyst coverage with oxygen atoms during the steam reforming reactions and enhance the H_2 and CO production rates [32-33].

Figure 5 shows the LHV values calculated using the gasification data. In accordance with the results presented above, C_4 catalyst (this catalyst showed highest production rates of hydrogen and carbon monoxide) increased the LHV by a factor of 1.93 compared to noncatalytic gasification.

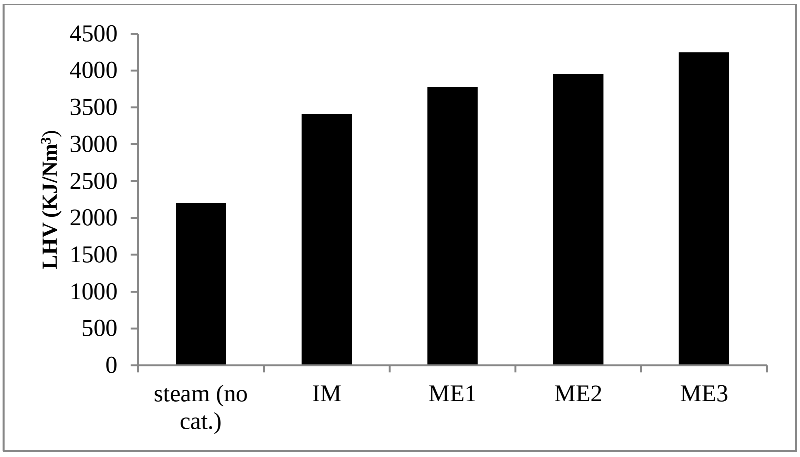

Figure 5 Comparison of LHV amounts between non-catalytic and catalytic gasification via steam reforming.

4. Conclusion

Hydrogen production from bagasse creates a promising future for development of a clean and accessible source of energy. The results showed that the efficiency of bagasse gasification in presence of steam increased, significantly. Catalytic steam gasification was performed in the presence Ni-Fe/γ-Al_2O_3 nanocatalysts prepared with impregnation and microemulsion techniques. Using the microemulsion technique especially at lower water to surfactant ratios, decreases the catalyst average particle size and increases the percentage dispersion and reduction of the catalyst. Also, the Ni-Fe/γ-Al_2O_3 catalyst prepared through the microemulsion technique with lowest W/S ratio (0.16) increases the hydrogen, CO yield, but decreases the light gaseous hydrocarbons yield.

References

[1] Tanksale A, Beltramini JN, Lu GQM. A review of catalytic hydrogen production processes from biomass. Renew Sustain Energy Rev 2010; 14:166–82.
[2] Asadullah M, Ito S, Kunimori K, Yamada M, Tomishige K.. Biomass gasification to hydrogen and syngas at low temperature: novel catalytic system using fluidized-bed reactor. J Catal 2002; 208:255–9.
[3] Dincer K. Lower emissions from biodiesel combustion. Energy Source Part A. 2008; 30:963–8.
[4] Yolcular S. Hydrogen production for energy use in European Union countries and Turkey. Energy Sour A 2009; 31:1329–37.
[5] Turner J, Sverdrup G, Mann MK, Maness PC, Kroposki B, Ghirardi M, Evans RJ. Renewables and hydrogen energy technologies for sustainable development. International Journal of Energy Research 2008; 32: 379–407.
[6] Arnavat MP, Bruno JC, Coronas A. Review and analysis of biomass gasification models. Renewable & Sustainable Energy Reviews 2010; 14: 2841–2851.
[7] Lu Y, Guo L, Zhang X, Chengmeng J. Hydrogen production by supercritical water gasification of biomass: explore the way to maximum hydrogen yield and high carbon gasification efficiency. International Journal of Hydrogen Energy 2012; 37:3177–3185.
[8] Vamvuka D. Bio-oil, solid and gaseous biofuels from biomass pyrolysis processes-an overview. International Journal of Energy Research 2011; 35:835–862.

[9] McKendry P. Energy production from biomass (part 1): overview of biomass. Bioresour Technol 2002; 83:37–46.

[10] McKendry P. Energy production from biomass (part 3): gasification technologies. BioresourTechnol 2002; 83:55–63.

[11] Lind, F., *et al.* Continuous Catalytic Tar Reforming of Biomass Derived Raw Gas Simultaneous catalyst Regenertation. Chalmers University of Technology 2011.

[12] Li C, Suzuki K. Tar property, analysis, reforming mechanism and model for biomass gasification-An overview. Renewable and Sustainable Energy Reviews 2009; 13: 594-604.

[13] Milne TA., Abatzoglou N, Evans RJ. Biomass Gasifier 'Tars': their nature, formation and conversion. NREL Technical Report (NREL/TP-570-25357), November 1998.

[14] Sutton D, Kelleher B, Ross JRH. Review of literature on catalysts for biomass gasification. Fuel Process Technol 2001; 73:155–73.

[15] Abu E-RZ, Bramer EA, Brem G. Review of catalysts for tar elimination in biomass gasification processes, Ind Eng Chem Res 2004; 43:6911–9.

[16] Kuln JN, Zhao Z, Felix LG, Slimane RB, Choi CW, Ozkan US. Olivine catalysts for methane- and tar-steam reforming. Applied Catalysis B: Environmental 2008; 81:14-26.

[17] Wang TJ, Chang J, Wu CZ, Fu Y, Chen Y. The steam reforming of naphthalene over a nickel-dolomite cracking catalyst. Biomass and Bioenergy 2005; 28:508-14.

[18] Baker EG, Mudge LK, Brown MD. Steam gasification of biomass with nickel secondary catalysts. Ind Eng Chem Res 1987; 26:1335–9.

[19] Leppälahti JK, Simell PA, Kurkela EA. Catalytic conversion of nitrogen compounds in gasification gas. Fuel Process Technol 1991; 29:43–56.

[20] Rasmussen FB, Sehested J, Teunissen HT, Molenbroek AM, Clausen BS. Sintering of Ni/Al_2O_3 catalysts studied by anomalous small angle X-ray scattering. Applied Catalysis A: General 2004, 267, 165-73.

[21] Kazama A., Sekine Y, Oyama K, Matsukata M, Kikuchi E. Promoting effect of small amount of Fe addition onto Co catalyst supported on α-Al_2O_3 for steam reforming of ethanol. Applied Catalysis A: General 2010; 383:96-101

[22] Torres JA, Llorca J, Casanovas A, Domínguez M, Salvadó J, Montané D. Steam reforming of ethanol at moderate temperature: Multifactorial design analysis of Ni/La_2O_3-Al_2O_3, and Fe- and Mn-promoted Co/ZnO catalysts. Journal of Power Sources 2007; 169:158.

[23] Dela Pena O'Shea VA, Nafria R, Ramírez de la Piscina P, Homs N. Development of robust Co-based catalysts for the selective H_2-production by ethanol steam-reforming. The Fe-promoter effect. International Journal of Hydrogen Energy 2008; 33:3601.

[24] Nedyalkova R, Casanovas A, Llorca J, Montané D. Electrophoretic deposition of Co–Me/ZnO (Me = Mn,Fe) ethanol steam reforming catalysts on stainless steel plates. International Journal of Hydrogen Energy 2009; 34:2591.

[25] Casanovas A, Roig M, De Leitenburg C, Trovarelli A, Llorca J. Ethanol steam reforming and water gas shift over Co/ZnO catalytic honeycombs doped with Fe, Ni, Cu, Cr and Na. International Journal of Hydrogen Energy 2010; 35:7690.

[26] Sun, J, Qiu, X, Wu, F, Zhu, W. from steam reforming of ethanol at low temperature over , and catalysts for fuel-cell application. Int. J. Hydrogen Energy 2005; 30: 437.

[27] Seok, S, Choi, S, Park, E, Han, S, Lee, J. Mn-Promoted Ni/Al_2O_3Catalysts for Stable Carbon Dioxide Reforming of Methane. J. Catal. 2002; 209:6.

[28] Kong M, Fei J, Wang S, Lu W, Zheng X. Influence of supports on catalytic behavior of nickel catalysts in carbon dioxide reforming of toluene as a model compound of tar from biomass gasification. BioresourTechnol 2011; 102:2004–8.

[29] Wang L, Li D, Koike M, Koso S, Nakagawa Y, Xu Y, Tomishige K. Catalytic performance and characterization of Ni-Fe catalysts for the steam reforming of tar from biomass pyrolysis to synthesis gas. Applied Catalysis A: General 2011; 392:248–255.

[30] Ansari M, Jafarian S, Tavasoli A, Karimi A, Rashidi M. Hydrogen rich gas production via nano-catalytic pyrolysis of bagasse in a dual bed reactor. JNGSE 2014; 19:279.
[31] Brammer IG, Bridgwater AV. The influence of feedstock drying on the performance and economics of a biomass gasifier-engine CHP System. Biomass and Bioenergy 2002; 22:271–81.
[32] Rapagná S, Latif A. Steam gasification of almond shells in a fluidized bed reactor: the influence of temperature and particle size on product yield and distribution. Biomass Bioenergy 1997; 12:281–8.
[33] Tomishige K, Kimura T, Nishikawa J, MiyazawaT, Kunimori K. Promoting effect of the interaction between Ni and CeO2 on steam gasification of biomass. K. Catal. Commun 2007; 8: 1074–9.