Application of Aspen Plus to Hydrogen Production from Alcohols by Steam Reforming: Effects of Reactor Temperature

Abdulwahab Giwa[1]andSaidat Olanipekun Giwa[2]

[1]Department of Chemical Engineering, Faculty of Engineering, Middle East Technical University, 06800, Ankara, Turkey
[2]Department of Chemical Engineering, Faculty of Engineering, Ankara University, 06100, Ankara, Turkey

ABSTRACT

This work has been carried out to apply Aspen Plus to investigate the effects of reactor temperature on the production of hydrogen by steam reforming process of methanol, ethanol, and glycerol. The steam reforming process used was modeled with the aid of Aspen Plus using equilibrium reactor and taking the overall reaction of the process involving each alcohol into consideration. In the modeling of the process using Aspen Plus, UNIQUAC Functional-group Activity Coefficients (UNIFAC) was employed as the property model. The variations of the alcohol conversions, the qualities (fractions) and the flow rates of the hydrogen obtained were studied. From the results obtained,it was revealed thatthe conversions of glycerol and methanol were better than that of ethanol at moderate reactor temperature while at high temperature, the conversions of the three of them were approximately 100%. Also, it was discovered from the qualities of the products thatthe alcohol that was able to give the highest mole, mass and volume fractions of hydrogen from the process carried out at high temperature was ethanol. Furthermore, the flow rates of the hydrogen obtained from the process gave observations similar to those of its fractions in the sense that, at high temperatures, ethanol was still the alcohol that produced the highest molar, mass and volumetric flow rates of hydrogen from the process. The meaningful results obtained that were found to be in good agreements with the information available in the literature have shown that Aspen Plus has been successfully applied to investigate the effects of reactor temperature on the steam reforming process of the alcohols considered.

Keywords: Hydrogen, steam reforming, alcohol, reactor temperature, Aspen Plus.

1. INTRODUCTION

Hydrogen(H_2) is nowadays considered as an alternative fuel and its use is gaining more and more importance as the environmental impacts of hydrocarbons become more evident. Its production is a subject of current interest for fuel cell applicationsas in automotive applications or electricity production; for instance in polymer electrolyte membrane fuel cells(PEMFC). Polymer electrolyte membrane fuel cells are considered to have the potential to provide a source of clean energy for automotive applications as an alternative to gasoline or diesel engines. Apart from those uses of hydrogen, it is also used as an important material in chemical synthesis and refinery for clean fuel production (Dave and Pant, 2011).

Basically, with the purpose of producing hydrogen for polymer electrolyte membrane fuel cells, the reforming of alcohols and hydrocarbons allows hydrogen production in situ, avoiding the problems of hydrogen storage and transportation (Ahmed and Krumpelt,2001; Damle, 2008; Löffler et al.,2003; Men et al., 2008; Telotte et al., 2008; Sáet al., 2011).It is well known that hydrogen can be produced in a fuel processor from available fuels ($C_nH_mO_p$) by means of steam reforming reaction. Feedstock availability, cost and by-products of the process (purity, quality and quantity of steam produced) are the controlling factors that play key roles in the technology chosen. Among the various fuels which can be converted to hydrogen, alcohols are the very promising candidates because they are easily decomposed in the presence of water and generate hydrogen rich mixtures, suitable for feeding fuel cells (Goula et al., 2004).Normally, the hydrogen required for the polymer electrolyte membrane fuel cells can be produced from the liquid organics like methanol, ethanol, glycerol, dimethyel ether, etc. (Llera et al., 2012).

Methanol offers several advantages for hydrogen production compared to other hydrocarbons (Patel and Pant, 2009).It is usually used as hydrogen source in steam reforming reaction. Liquid methanol is easy to store and transport at room temperature. Furthermore, it has high hydrogen-carbon ratio and absence of carbon-carbon bonds (Fu and Wu, 2007).Considering ethanol, it presents several advantages in relation to natural availability, storage and handling safety. Its molecule produces 3 molecules of hydrogen, it is a non-toxic liquid at room temperature and it is chemically stable. It can be produced renewably from several biomass sources, including energy plants, waste materials from agro industries or forestry residue materials, organic fraction of municipal solid waste, etc. Besides, the bio-ethanol-to-hydrogen system has the significant advantage of being nearly CO_2 neutral, since the produced carbon dioxide is consumed for biomass growth, thus offering a nearly closed carbon loop. Among the various processes and primary fuels that have been proposed in hydrogen production for fuel cell applications, ethanol steam reforming is one of the most attractive of them (Klouz etal., 2002; Llera et al., 2012).Meanwhile, significant amount of glycerol is produced as a by-product during bio-diesel production by transesterification of vegetable oils, which are available at low cost in large supply from renewable raw materials. The promising way to utilize this diluted glycerol aqueous solution is to use it to producehydrogen by steam reforming (Zhang et al., 2007). Among the various renewable feedstock sources, glycerol is an alternative because it has relatively high hydrogen content, it is non-toxic, and its storage and handling is safe. It is mainly produced as a byproduct of biodiesel production, but it can also come from the fermentation of sugars or the conversion of lignocellulose. Some processes of hydrogen production from glycerol are currently under study as the steam reforming, the aqueous phase reforming and the partial oxidation or autothermal reforming (Pompeo et al., 2011).

Generally, chemical storage of hydrogen in liquid fuels is considered to be an advantageous option for delivering hydrogen. It can be seen that the different alcohols (methanol, ethanol and glycerol) mentioned so far have different advantages offered in the production of hydrogen using steam reforming process. Steam reforming has the highest efficiency for hydrogen production among other alternatives such as partial oxidation or auto-thermal reforming (Soyal-Baltacıoğlu, 2008). It is one of the most used reactions in hydrogen production. It is highly endothermic and low pressure favors selectivity to hydrogen (Pompeo et al., 2011).The reforming of oxygenated hydrocarbons (methanol, ethanol and glycerol) requires considerably less energy per mole of H_2 formed than the reforming of saturated hydrocarbons and produces mostly CO_2. Investigation of hydrogen production from ethanol is fairly new. Ethanol steam reforming proceeds at higher temperatures (350-900 ^oC) compared to that of methanol (200-400 ^oC) on account of its C-C bond, and at relatively high water-to-ethanol ratios (Soyal-Baltacıoğlu, 2008).

The investigation of the effects of some factors like the reaction temperature on the steam reforming process of alcohols can actually be investigated by carrying out the simulations of the process using the different alcohols to confirm what has been published in the literature concerning it. Up till now,very scarce researches have been come across in the literature that have applied process simulator(s) to the steam reforming process of alcohols for the production of hydrogen. However, some simulation studies have been carried out on this process. For instance, Ma et al. (1996) carried out the simulation studies of autothermal reactor system for hydrogen production from methanol steam reforming. Gonzo (2008) presented a simple, precise and fast procedure to simulate monolith reactors where methanol steam reforming reaction was accomplished. Iordanidis et al. (2006) used SIMSCI Pro II process simulator to investigate a concept of sorption-enhanced steam reforming of bio-oil/biogas for electricity and heat generation by phosphoric acid fuel cells. Pan and Wang (2005) carried out the modeling of a compact plate-fin reformer for methanol steam reforming in fuel cell systems. Uriz et al. (2011) studied a three-dimensional computational fluid dynamics (CFD) simulation study of ethanol steam reforming in microreactors with square channels. Chein et al. (2013) carried out a study on the numerical simulation of the performance of mini-scale reactors for hydrogen production coupled with liquid methanol/water vaporizer, methanol/steam reformer, and methanol/air catalytic combustor. Silva et al. (2009) simulated and optimized hydrogen production by autothermal reforming of glycerol. Considering the past researches discovered so far on the simulations of steam reforming of alcohols, it was realized that no work has applied Aspen Plus to this process.

Therefore, this work has been carried out to fill the gap highlighted above by using Aspen Plus to investigate how the reactor temperatures affect the conversion, the qualities and the flow rates of hydrogen obtained from the steam reforming of three different alcohols (methanol, ethanol and glycerol).

2. PROCEDURE

The process model of the steam reforming of the alcohols (methanol, ethanol and glycerol) investigated in this work, and developed with the aid of Aspen Plus (Aspen, 2012), is as shown in Figure 1 below. As can be seen from the figure, the process had two feed streams (water and alcohol) that were fed into the mixerplaced before the reactorat the same flow rates of 45 mL/min and at the same temperaturesand pressuresof 25 ^oC and 1 atm, respectively.

The pressure of the mixer was set to 0 atmbecause it was just used to mix the two liquids involved in the process before entering the reactor. Also, the valid phases of the mixer were vapor and liquid, even though no vapor was expected as part of the outputs of the mixerat the conditions used.

The temperature of the equilibrium reactor employed was varied from 30 to 1100 ^oC to investigate the qualities of the product using each of the three alcohols at a time as one of the feeds of the process. Actually, the term "steam reforming" would imply that the temperature of the reactor be at least 100 ^oC at which condition that the liquid water would be in vapor form. However, in order to actually have good and wide insights into the variations of the variables (alcohol conversion, the qualities and the flow rates of hydrogen produced) that were investigated with the variations in the temperature of the reactor, low temperatures of the reaction were as well considered.

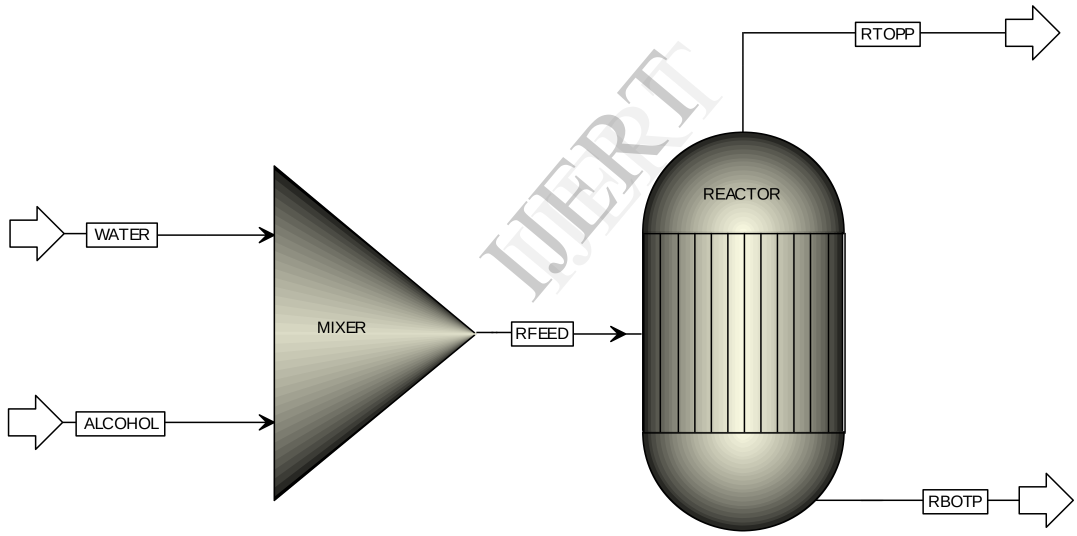

Figure 1. Aspen plus model of alcohol steam reforming process for the production of hydrogen

The reactions involved in the process were modeled as equilibrium types by considering the overall reactions of each of the processes involving the three alcohols.

For the steam reforming process involving methanol, the expression of the chemical reaction is given as:

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2 \quad (1)$$

while for that involving ethanol, the chemical reaction occurring in the reactor is written as:

$$C_2H_5OH + 3H_2O \leftrightarrow 2CO_2 + 6H_2 \quad (2)$$

and, finally, for the one between glycerol and water, the chemical expression is given as:

$$C_3H_8O_3 + 3H_2O \leftrightarrow 3CO_2 + 7H_2 \quad (3)$$

After the modeling and the simulations of the developed Aspen Plus model of the process using the three alcohols at the different temperatures considered, the conversion of each of the alcohol used, the qualities and the flow rates of the hydrogen produced by each of them were plotted against the temperatures to see their variations graphically.

3. RESULTS AND DISCUSSIONS

This work was actually carried out to study the steam reforming of three different alcohols using the process model developed with the aid of Aspen Plus. The three alcohols considered in this work were methanol, ethanol and glycerol. Apart from that, being steam reforming, the least reactor temperature was actually supposed to be 100 ^{o}C, but the investigations of the reactions were carried out starting from 30 ^{o}C, as mentioned before, just to have wide insights of the behavior of the process with liquid water also. All in all, the reactor temperature was varied for each of the alcohols from 30 to 1100 ^{o}C. The relationships between the conversions of the alcohols and the reactor temperature were first studied. After that, the variations of the mole, mass and volume fractions of hydrogen obtained from the alcohols were considered, and finally investigated were the amounts per unit time (in terms of mole, mass and volumetric flow rates) of hydrogen obtained from the process using each of the alcohols.

Shown in Figure 2 are the conversions obtained from the alcohols as a function of the reactor temperature. As can be seen from the figure, at low temperature, the conversion obtained from methanol was very low while that obtained from ethanol was approximately zero, but glycerol was able to give a conversion of as high as approximately 98%, even at the chosen initialreaction temperature (30 ^{o}C). This was an indication that, among the alcohols studied, glycerol was the only one favored very well by low reactor temperature, followed by methanol and the least favored by low reactor temperature was found to be ethanol.

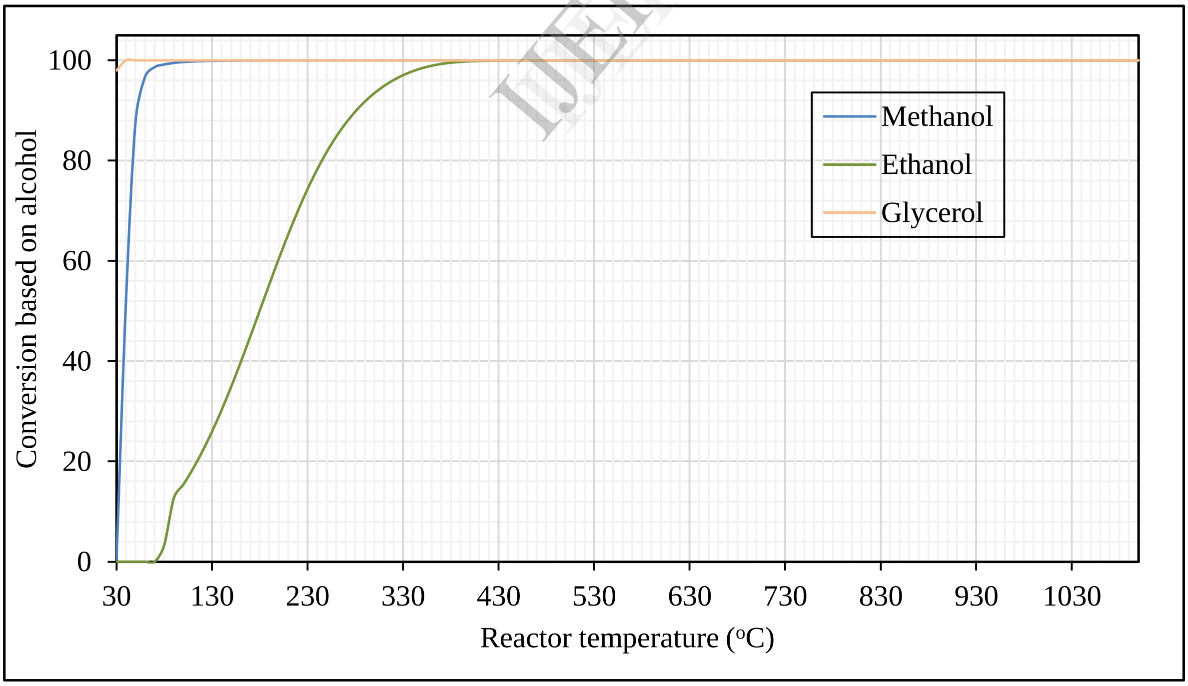

Figure 2. Conversion of alcohols obtained at different temperatures

According to the results obtained, as the reactor temperature was varied, the conversion of glycerol was the first to become 100% while the last one was that of ethanol. Specifically, at the reactor temperature of about 380 ^{o}C, the conversions of the three alcohols were discovered to be approximately 100%. The good performances, in terms of conversions, observed from glycerol and methanol were found to be in agreement with the information availablein the literature because according to Soyal-Baltacıoğlu (2008), ethanol steam reforming proceeds at higher temperaturescompared to that of methanol.

In Figure 3, the mole fractions of the hydrogen obtained from the steam reforming of the alcohols are shown. According to the figure, it was seen that glycerol was able to give the stable highest mole fractions of hydrogen atmoderate steam reforming temperatures (70 – 200 ^{o}C). At that particular temperature range, the mole fraction of the hydrogen obtained from ethanol was the least. However, as from a highreactor temperature of about 250 ^{o}C and further, ethanol was the alcohol that could give the highest mole fraction of hydrogen among the alcohols considered in this work. One interesting thing noticed in the mole fraction of hydrogen obtained from ethanol was that, at low temperature, there was a kind of high mole fraction given but this point was not stable because it immediately decreased before rising again to become stable and constant at high reactor temperatures. This has shown that the steam reforming of ethanol can only be achieved in a stable manner at high temperature greater than those required for the reforming of both methanol and glycerol.

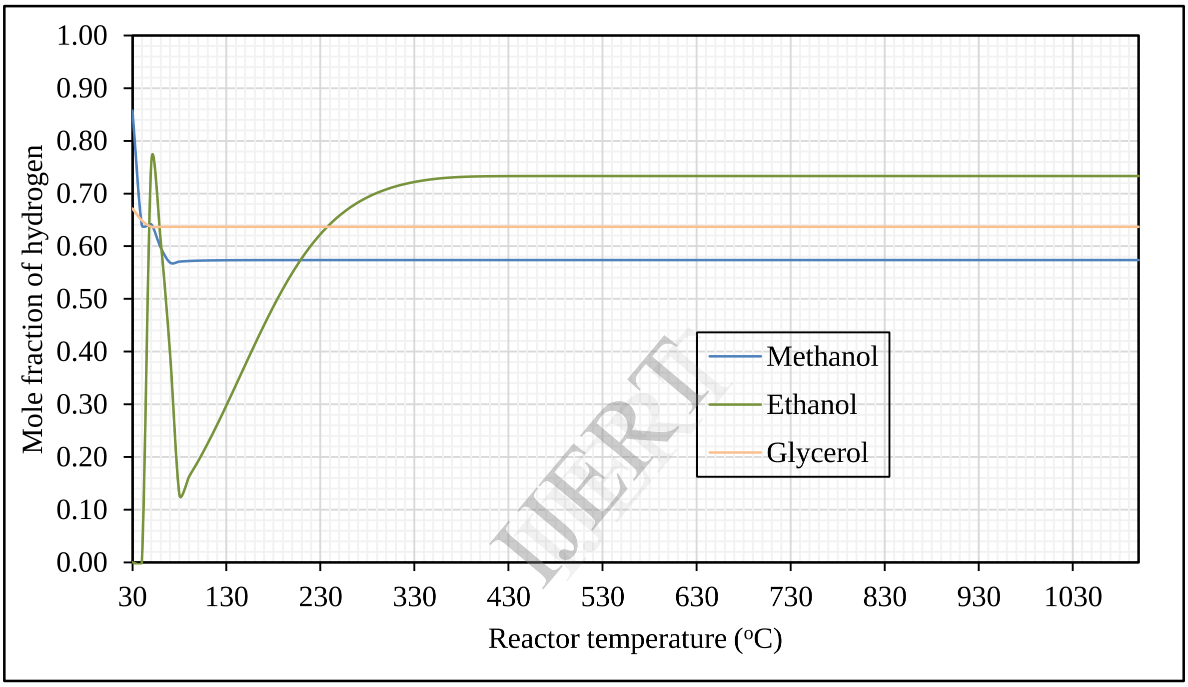

Figure 3. Mole fraction of hydrogen obtained from the alcohols obtained at different temperatures

Further considering the mass fraction of hydrogen obtained from the three different alcohols considered, shown in Figure 4 is the graph showing the changes in the hydrogen mass fractions given by the alcohols as functions of the reactor temperature of the steam reforming process. The relationships obtained from the figure were found to be very similar to those obtained from the graph of the mole fractions of hydrogen, given in Figure 3. As can be seen from the figure of the mass fraction of hydrogen (Figure 4), at low to moderate reactor temperatures, glycerol was able to give the hydrogen with the highest mass fraction followed by methanol and the least mole fraction of hydrogen was obtained from ethanol, but at high temperatures, the highest mass fraction of hydrogen was obtained from the steam reforming of ethanol followed by glycerol and, in this case, the least hydrogen was given by methanol. As also seen from the results shown in Figure 4, the differences between the mass fractions of the hydrogen obtained from the steam reforming of methanol and glycerol were found to be less than their differences in the results of the mole fractions of hydrogen (see Figure 3).

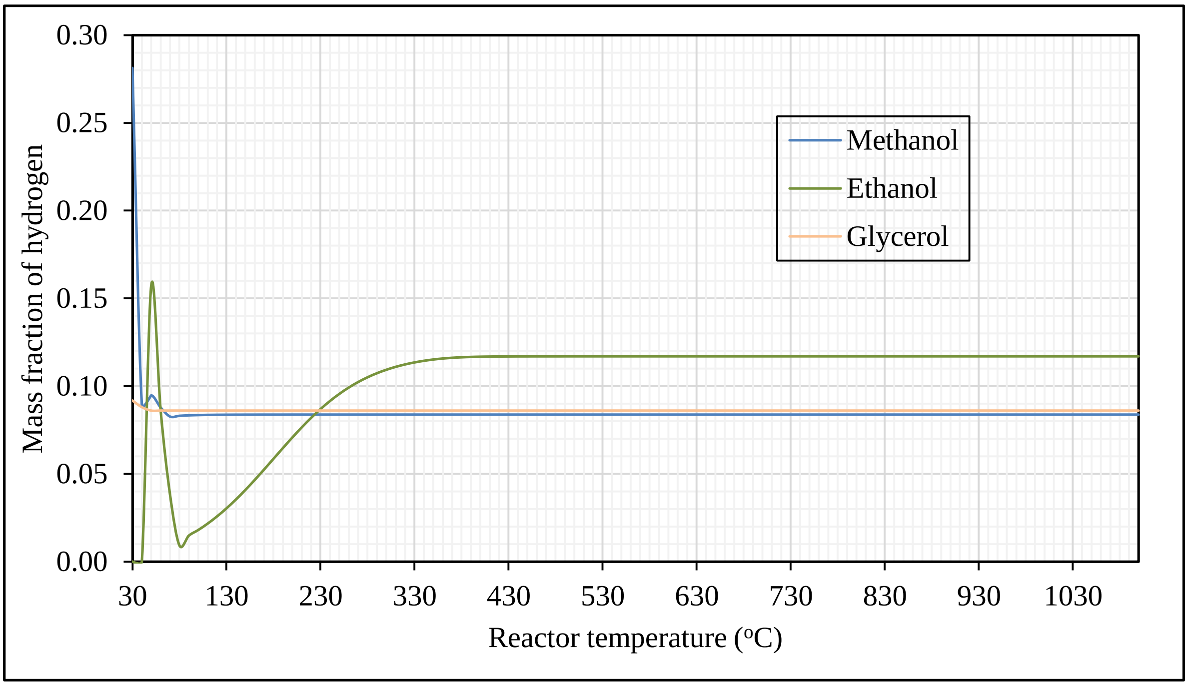

Figure 4. Mass fraction of hydrogen obtained from the alcohols obtained at different temperatures

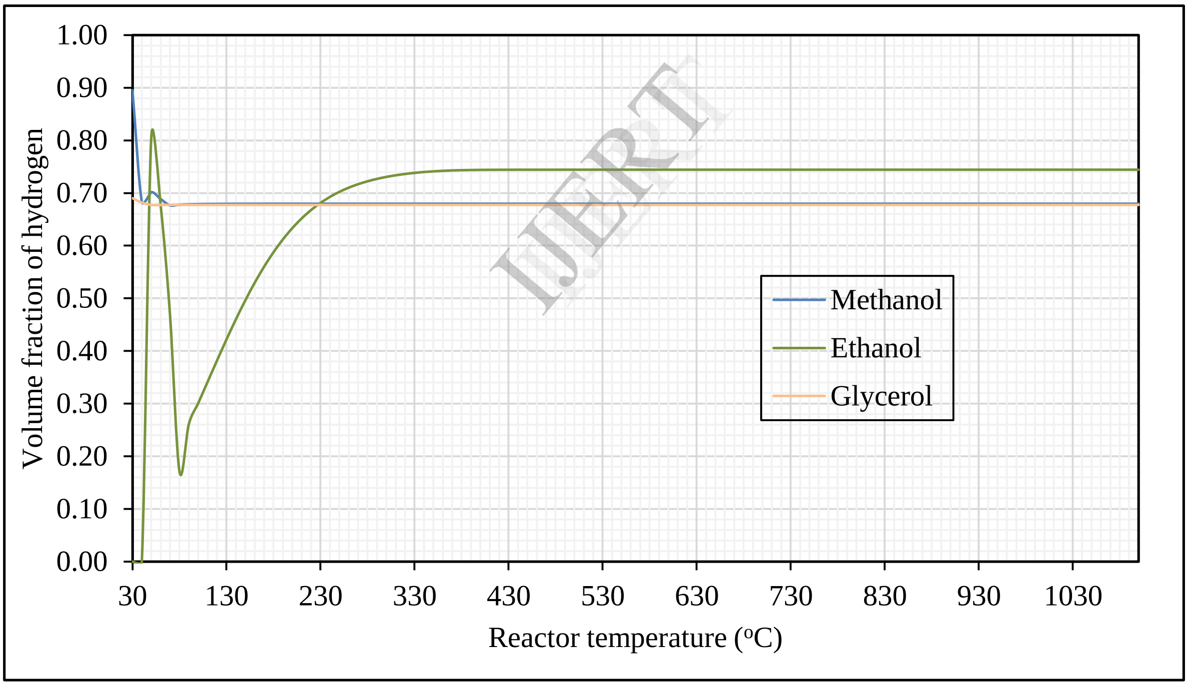

Figure 5. Volume fraction of hydrogen obtained from the alcohols obtained at different temperatures

The volume fractions of hydrogen obtained from the alcohols shown in Figure 5 also revealed ethanol to be the alcohol that gave the highest volume fraction of hydrogen at high temperatures. At low temperatures, the behaviors of the volume fractions of hydrogen from the alcohols, especially those from methanol and ethanol, were discovered not to be not stable. This behaviors were found not to be surprising because the reactions occurring at low temperature, especially at reactor temperature less than the boiling point of water, real steam reforming could not be said to be steam reforming. At moderate reactor temperatures, the volume fractions of hydrogen obtained from methanol and glycerol were found to be very close to one another and higher than that obtained from ethanol. At high reactor temperatures, the behaviors of the volume fractions of hydrogen given by methanol and glycerol were still found to be the same as those obtained at moderate temperatures, but, this time around, the highest volume fraction of hydrogen was found to be given by ethanol.

Apart from considering the fractions of the desired product (hydrogen) of the steam reforming of the three different alcohols (methanol, ethanol and glycerol), the rates (molar flow rate, mass flow rate and volumetric flow rate) at which the hydrogen given by the process using each of the alcohols was collected from the reactor were also investigated and the results of these investigations are as given in Figures 6 – 8.

The plots of the molar flow rates of hydrogen obtained from the steam reforming of the alcohols are given in Figure 6. As can be seen in the figure, the molar flow rates of hydrogen obtained from the three alcohols were found to increase with increase in reactor temperature. However, at low to moderate reactor temperature, the molar flow rate of hydrogen obtained from ethanol was approximately zero; that obtained from methanol also at very low temperature was as well very close to zero. At high temperatures, the highest molar flow rates of hydrogen was obtained when ethanol was used as the alcohol for the steam reforming process. At both low and high temperature, hydrogen production was found to be favored with glycerol than with methanol. Of course, these results obtained from the molar flow rates of hydrogen given by the alcohols were found to be in support of the observations made in the results of the mole fractions of the hydrogen production.

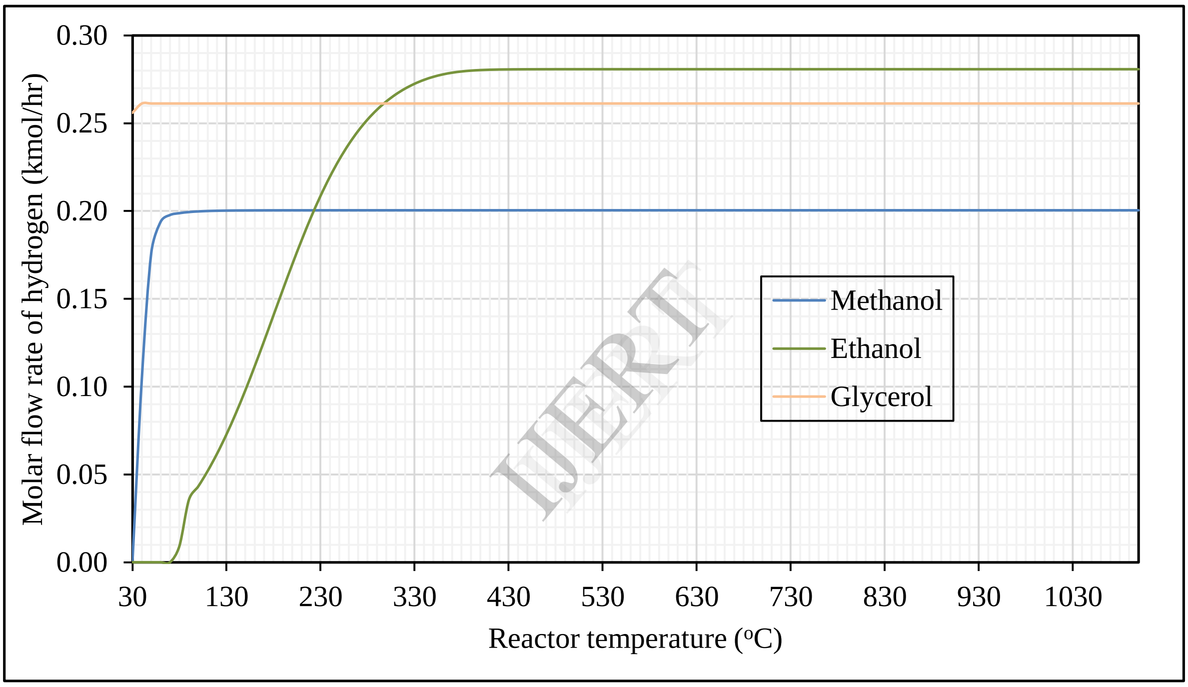

Figure 6. Molar flow rate of hydrogen obtained from the alcohols obtained at different temperatures

Also considered in this work and the results of which are shown in Figure 7 were the mass flow rates of hydrogen obtained from the steam reforming of alcohols investigated in this study. The observations made in this case were found to be similar to those that were observed in the case of the molar flow rates of hydrogen (Figure 6) given by the steam reforming of the alcohols. As can be seen from the figure, at low temperature, the highest mass flow rate of hydrogen was obtained from glycerol, but at very high temperature, hydrogen was given with highest mass flow rate by the steam reforming of ethanol.

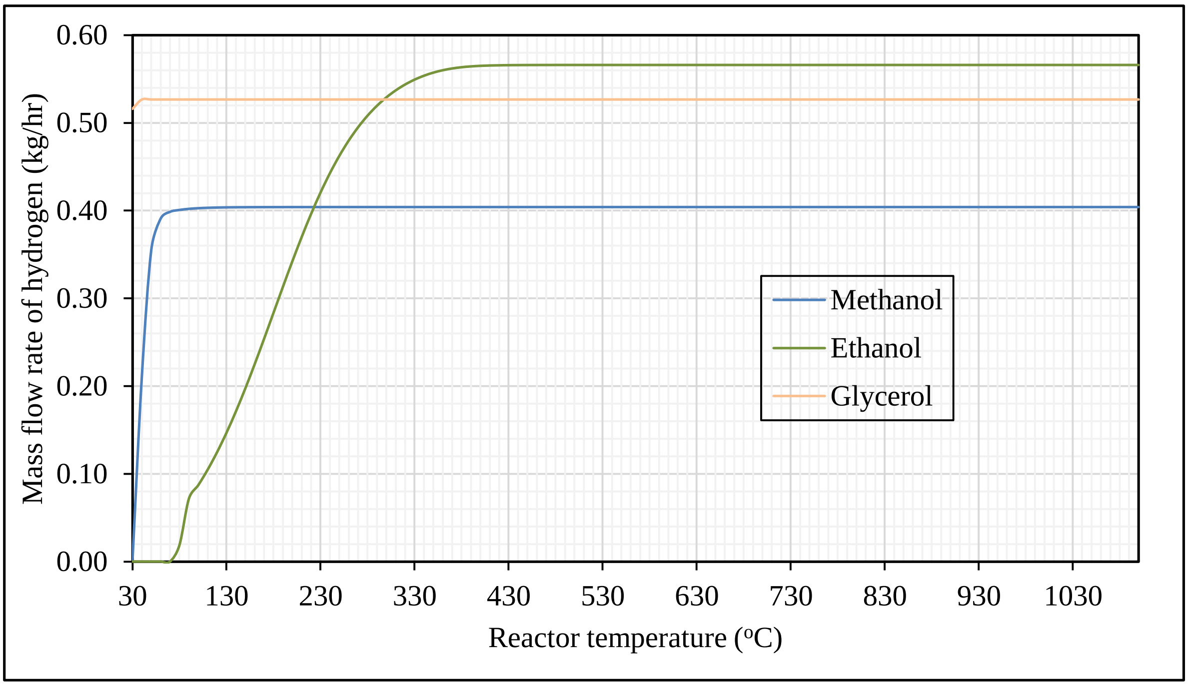

Figure 7. Mass flow rate of hydrogen obtained from the alcohols obtained at different temperatures

Shown in Figure 8 are the volumetric flow rates of hydrogen obtained as the product of the steam reforming of methanol, ethanol and glycerol. The observations made in this figure were discovered to be similar to the ones made from the results of the molar and the mass flow rates of hydrogen given by the steam reforming of the alcohols, and discussed before. Again, at low and moderate temperatures, hydrogen production from steam reforming was favored well using glycerol as the alcohol feed, but at high temperatures, the highest volumetric flow rates of hydrogen was obtained using ethanol as the alcohol feed of the steam reforming.

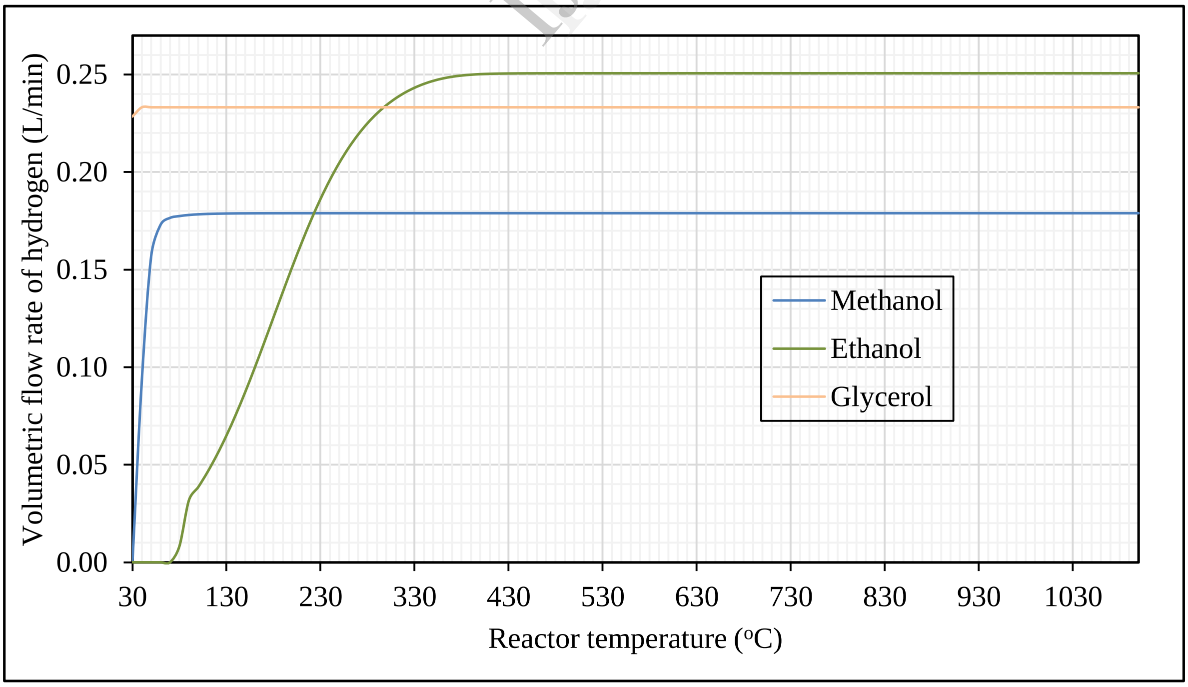

Figure 8. Volumetric flow rate of hydrogen obtained from the alcohols obtained at different temperatures

It has been seen from the flow rates of hydrogen obtained from the steam reforming of methanol, ethanol and glycerol and discussed above that the behaviors of molar, mass and volumetric flow rates of hydrogen given by the three alcohols considered were very similar to one another in the sense that, in all the flow rates of hydrogen obtained from the three alcohols investigated, that obtained from glycerol was favored at low to moderate reactor temperature while at high temperature, the one given by the steam reforming of ethanol was favored.

4. CONCLUSIONS

The results of the alcohol conversions obtained from this work that has been carried out to study the effect of reactor temperature on the steam reforming of methanol, ethanol and glycerol have revealed that, at moderate temperature, the conversions of glycerol and methanol were better than that of ethanol, but at high temperature, the conversions of the three alcohols were approximately 100%. In addition, the results of the qualities of the products revealed that, at high temperature, the alcohol that was able to give the highest mole, mass and volume fraction of hydrogen from the process was ethanol. Similar observations were made in the case of the flow rates of the hydrogen obtained from the process because, at high temperatures, ethanol was the alcohol that produced the highest molar, mass and volumetric flow rates of hydrogen from the steam reforming process investigated. The variations obtained from the variables considered with respect to the reactor temperature were found to be in agreement with the information available in the literature. Therefore, Aspen Plus has been successfully applied to investigate the effect of reactor temperature on the steam reforming process of the alcohols considered.

ACKNOWLEDGEMENTS

The authors wish to acknowledge and appreciate the supports received from the Prime Ministry of The Republic of Turkey, Presidency for Turks Abroad and Related Communities for their Postdoctorate and Doctorate programmes, respectively.

NOMENCLATURES

RBOTP	Reactor bottom product
RFEED	Reactor feed
RTOPP	Reactor top product
UNIFAC	UNIQUAC Functional-group Activity Coefficients model

REFERENCES

[1] Ahmed, S., & Krumpelt, M. (2001). Hydrogen from hydrocarbon fuels for fuel cells. *International Journal of Hydrogen Energy*, *26*, 291–301.

[2] Aspen. 2012. Aspen Plus. Aspen Technology, USA.

[3] Chein, R., Chen, Y.-C., & Chung, J. N. (2013). Numerical study of methanol–steam reforming and methanol–air catalytic combustion in annulus reactors for hydrogen production. *Applied Energy*, *102*, 1022–1034.

[4] Damle, A. S. (2008). Hydrogen production by reforming of liquid hydrocarbons in a membrane reactor for portable power generation – Modelsimulations. *Journal of Power Sources*, *180*(1), 516–529.

[5] Dave, C. D., & Pant, K. K. (2011). Renewable hydrogen generation by steam reforming of glycerol over zirconia promoted ceria supported catalyst. *Renewable Energy*, *36*(11), 3195–3202.

[6] Fu, C., & Wu, J. (2007). Mathematical simulation of hydrogen production via methanol steam reforming using double-jacketed membrane reactor. *International Journal of Hydrogen Energy*, *32*(18), 4830–4839.

[7] Gonzo, E. (2008). Hydrogen from methanol-steam reforming. Isothermal and adiabatic monolith reactors' simulation. *International Journal of Hydrogen Energy*, *33*(13), 3511–3516.

[8] Goula, M. a., Kontou, S. K., & Tsiakaras, P. E. (2004). Hydrogen production by ethanol steam reforming over a commercial Pd/γ-Al_2O_3 catalyst. *Applied Catalysis B: Environmental*, *49*(2), 135–144.

[9] Iordanidis, a, Kechagiopoulos, P., Voutetakis, S., Lemonidou, a, & Vasalos, I. (2006). Autothermal sorption-enhanced steam reforming of bio-oil/biogas mixture and energy

generation by fuel cells: Concept analysis and process simulation. *International Journal of Hydrogen Energy*, *31*(8), 1058–1065.

[10] Klouz, V., Fierro, V., Denton, P., Katz, H., Lisse, J. ., Bouvot-Mauduit, S., & Mirodatos, C. (2002). Ethanol reforming for hydrogen production in a hybrid electric vehicle: process optimisation. *Journal of Power Sources*, *105*(1), 26–34.

[11] Llera, I., Mas, V., Bergamini, M. L., Laborde, M., & Amadeo, N. (2012). Bio-ethanol steam reforming on Ni based catalyst. Kinetic study. *Chemical Engineering Science*, *71*, 356–366.

[12] Löffler, D. G., Taylor, K., & Mason, D. (2003). A light hydrocarbon fuel processor producing high-purity hydrogen. *Journal of Power Sources*, *117*(1-2), 84–91.

[13] Ma, L., Jiang, C., Adesina, A. A., Trimm, D. L., & Wainwright, M. S. (1996). Simulation studies of autothermal reactor system for H_2 production from methanol steam reforming. *The Chemical Engineering Journal and the Biochemical Engineering Journal*, *62*(2), 103–111.

[14] Men, Y. (2008). A complete miniaturized microstructured methanol fuel processor/fuel cell system for low power applications. *International Journal of Hydrogen Energy*, *33*(4), 1374–1382.

[15] Pan, L., & Wang, S. (2005). Modeling of a compact plate-fin reformer for methanol steam reforming in fuel cell systems. *Chemical Engineering Journal*, *108*(1-2), 51–58.

[16] Patel, S., & Pant, K. K. (2009). Kinetic modeling of oxidative steam reforming of methanol over $Cu/ZnO/CeO_2/Al_2O_3$ catalyst. *Applied Catalysis A: General*, *356*(2), 189–200.

[17] Pompeo, F., Santori, G. F., & Nichio, N. N. (2011). Hydrogen production by glycerol steam reforming with Pt/SiO_2 and Ni/SiO_2 catalysts. *Catalysis Today*, *172*(1), 183–188.

[18] Sá, S., Sousa, J. M., & Mendes, A. (2011). Steam reforming of methanol over a $CuO/ZnO/Al_2O_3$ catalyst, part I: Kinetic modelling. *Chemical Engineering Science*, *66*(20), 4913–4921.

[19] Silva, G., & Fereira, A. (2009). Simulation and optimization of H_2 production by autothermal reforming of glycerol. *Computer Aided Chemical Engineering*, *27*, 987–992.

[20] Soyal-Baltacıoğlu, F., Aksoylu, a. E., & Önsan, Z. I. (2008). Steam reforming of ethanol over Pt–Ni Catalysts. *Catalysis Today*, *138*(3-4), 183–186.

[21] Telotte, J. C., Kern, J., & Palanki, S. (2008). Miniaturized methanol reformer for fuel cell powered mobile applications. *International Journal Of Chemical Reactor Engineering,6*, 1–13.

[22] Uriz, I., Arzamendi, G., López, E., Llorca, J., & Gandía, L. M. (2011). Computational fluid dynamics simulation of ethanol steam reforming in catalytic wall microchannels. *Chemical Engineering Journal*, *167*(2-3), 603–609.

[23] Zhang, B., Tang, X., Li, Y., Xu, Y., & Shen, W. (2007). Hydrogen production from steam reforming of ethanol and glycerol over ceria-supported metal catalysts. *International Journal of Hydrogen Energy*, *32*(13), 2367–2373.