

Production of Synthesis Gases from Ethanol Steam Reforming Process

Menderes Levent¹, Murat Ağbaba², Yusuf Şahin²

¹Department of Chemical Engineering, Faculty of Engineering, Uşak University, Uşak, Turkey

²Department of Physics, Faculty of Science and Art, Atatürk University, Erzurum, Turkey

Email: menderes.levent@usak.edu.tr

Received 12 July 2016; accepted 14 August 2016; published 17 August 2016

Copyright © 2016 by authors and Scientific Research Publishing Inc.

This work is licensed under the Creative Commons Attribution International License (CC BY).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

In this study, the production of synthesis gases has been purposed under between 250°C - 700°C and 1 - 2 bars pressures. The research was conducted over a commercial BASF catalyst and a laboratory prepared catalyst. The catalyst has a content of different substances including basically NiO/Al₂O₃ and some additional (Ca, Mg, Cr, Si). The experimental measurements were carried out within a recently developed experimental equipment which can be operated up to 1200° and 1 to 3 bars pressures. The study was conducted over a commercial BASF catalyst and a laboratory prepared catalyst under different ethanol/water ratios, temperatures, and catalyst loads. Under the condition when ethanol/water ratios were decreased from 1/2 to 1/10, it was observed that hydrogen ratios increased in exit gas composition of the reactor. With increments in catalyst loads from 1 to 5 grammes, hydrogen ratios in exit gas composition gradually increased. Reaction of ethanol-steam reforming started nearly at 300°C, and when temperature increments continued further up to 700°C, hydrogen yields in exit gas compositions of the reactor increased significantly to a range of 70% - 80%. In the case of using commercial BASF catalyst, hydrogen ratios in exit gas composition were found slightly higher than laboratory prepared catalyst. According to our observations, life time of laboratory prepared catalyst was found higher than the commercial BASF catalyst. In this study which kinetic measurements were applied, some kinetic parameters of ethanol-steam reaction were calculated. The mean activation energy of ethanol consumptions at 573°K - 973°K was found as 26.87 kJ/mol, approximately. All kinetic measurements were analyzed with a first order reaction rate model. In this study, some diffusion limitations existed, however, overall reaction was chemically controlled.

Keywords

Ethanol-Steam Reforming, Preparation of Catalysts, Hydrogen Production, Synthesis Gas, Coke Formation

1. Introduction

Due to high demand in energy consumption and the recent improvements in fuel cell technology, it increases the synthesis gas production requirements from the different fuel sources. Hydrogen from steam reforming of ethanol was studied by F. J. Marino *et al.* [1]. The effect of copper loading and calcination temperature on the structure of the catalyst were studied. In order to maximize hydrogen production, copper loading, calcination temperature and catalyst preparation were purposed [1]. A thermodynamic analysis of hydrogen production by steam reforming of ethanol was studied by I. Fishtik *et al.* [2]. A simple algorithm was purposed to rationalize the effect of process variables on steam reforming of ethanol. At or above 700°K - 800°K and higher water/ethanol ratios, the desired reaction of ethanol steam reforming reaction can be predominated [2].

A two-layer fixed bed catalytic reactor for syngas production by steam reforming of ethanol was reported by V. V. Galvita *et al.* [3]. In recommended concept, ethanol is, firstly, converted to a mixture of methane, carbon oxides and hydrogen and then this mixture is converted to syngas [3]. Hydrogen production by catalytic ethanol steam reforming was studied by A. Therdthianwong *et al.* [4]. In this study, experiments were conducted in a fixed bed reactor on Ni/Al₂O₃ catalyst. As W/F ratio and temperatures increase, the H₂ yields increase in reactor exit. For rate expression, the power-law rate expression was determined.

Hydrogen generation by steam reforming of methanol over copper-based catalysts for fuel cell applications was studied by B. Lindström *et al.* [5]. In the research, it was concluded that copper-based catalysts were effective for the steam reforming of methanol. The use of copper content and promoters (Cr, Zn, Zr) played an important role in converting selectively methanol at low temperatures (180°C - 320°C). Optimisation of ethanol reforming for hydrogen production in a hybrid electric vehicle was purposed by V. Klouz *et al.* [6]. A detailed kinetic scheme of the ethanol was discussed as a function of the temperature and the role of oxygen in the reaction selectivity and coke formation was investigated.

H₂ production for molten carbonate fuel cell from steam reforming of ethanol was studied by S. Freni *et al.* [7]. Results of the study indicated that Ni-MgO catalytic systems were adequate properties for efficient hydrogen production by ethanol steam reforming. Conversion of hydrocarbons and alcohols for fuel cells was studied by Joensen *et al.* [8]. Pure hydrogen is the recommended fuel due to simplicity in design, low cost and high efficiency [8].

The reformation of biomass-derived ethanol to a hydrogen-rich gas stream was studied by A. N. Fatsikostas [9]. The influence of reaction temperature, water to ethanol ratio and space velocity was conducted. Hydrogen production by auto-thermal reforming of ethanol on Rh/Al₂O₃ catalyst was studied by S. Cavallaro [10]. The results have indicated that if the optimum range where ethanol conversion is 100% is reached, the productions of CH₄ and CO go down and hydrogen yield reaches to the maximum range before decreasing.

The catalytic performance of supported noble metal catalysts for the steam reforming of ethanol has been investigated by D. K. Liguras *et al.* [11] in the temperature range between 600°C - 850°C. They concluded that supported Rh catalysts were significantly more active and were selective for ethanol steam reforming reaction. The metal-support interaction triggering Cu-Ni-K/ γ -Al₂O₃ supported catalysts for ethanol steam reforming formation of hydrotalcite-type compounds was studied by F. Marino *et al.* [12].

The function of the steam reforming of ethanol on 5% Rh/Al₂O₃ catalyst in producing H₂ to feed a molten carbonate fuel cell was investigated by S. Cavallaro *et al.* [13]. The ethanol steam reforming on Ni/ γ -Al₂O₃ catalyst at temperature between 573 and 773°K was studied by J. Comas *et al.* [14] and an overall reaction scheme as a function of temperature was purposed. They concluded that high temperatures (above 773°K), higher water/ethanol ratios (about 6:1) promote high hydrogen yield on Ni/ γ -Al₂O₃ catalyst.

The effects of alkali additions (e.g. Li, Na, K) on the behavior of Ni/MgO catalyst in the bio-ethanol steam reforming have been investigated by F. Frusteri *et al.* [15]. The effects of catalyst synthesis method (e.g. precipitation, coprecipitation and impregnation), Ni loading and reduction temperature on the characteristics and performance of Ni/Al₂O₃ catalysts were studied by A. J. Akande *et al.* [16] with the aim of investigating the reforming of crude ethanol for H₂ production. As a result, it was found out that precipitation catalysts were more reducible than coprecipitation and impregnation catalysts. Catalyst with 15% Ni loading trigger the best crude ethanol conversion [16].

By means of ultra high vacuum temperature which is programmed desorption conditions, the influence of oxygen on the decomposition of ethanol over rhodium and single crystal surfaces were studied by E. Vesselli *et al.* [17]. On the contrary, excess of oxygen lead to a strong reduction of hydrogen concentration in the reaction

products. Influence of the addition of promoters to steam reforming catalysts was studied by J. S. Lisboa *et al.* [18]. The catalyst was Ni/ α -Al₂O₃ which was modified by the addition of promoters (Mg and Ca) to improve their stability and selectivity. The results of reaction demonstrated that there is an increase in the reforming activity by the presence of promoters. A series of CuNiZnAl-multicomponent mixed metal oxide catalysts was used in the oxidative steam reforming of bio-ethanol by S. Velu *et al.* [19]. As a result, Cu²⁺ was fully reduced, while Ni²⁺ and Zn²⁺ were partially reduced.

Ethanol steam reforming over Mg_xNi_{1-x}Al₂O₃ spinel oxide-supported Rh catalysts was studied by F. Aupretre *et al.* [20]. In this study, the effects of the precursors which were used in the support and catalyst preparation were conducted. Nitrate precursors were the most obtained acidic materials and had the poorest stability one. The catalyst prepared with Rh chloride were moderately acidic, and they were very active and stable. Ethanol steam reforming consists of three main reactions accounting for the formation of H₂, CO₂, CO, and CH₄ [20]:



Three main parameters may affect the H₂ yield at equilibrium (Y_{H_2}): temperature (T), total pressure (P), initial H₂O/ethanol molar ratio (F_{WE}). Y_{H_2} increases with T and F_{WE} and decreases with pressure [20].

$$X_{\text{EtOH}} = \frac{n_{\text{EtOH}}^{\text{in}} - n_{\text{EtOH}}^{\text{out}}}{n_{\text{EtOH}}^{\text{in}}} \times 100 \quad \text{and} \quad Y_{\text{H}_2} = \frac{n_{\text{H}_2}^{\text{out}}}{n_{\text{EtOH}}^{\text{in}} - n_{\text{EtOH}}^{\text{out}}}. \quad (4)$$

The influence of the nature of the metal on the performance of cerium oxide supported catalyst in the partial oxidation of ethanol was studied by L. V. Mattos and co-worker [21]. The results which were obtained from the study demonstrated that nature of the metal strongly affected the product distribution.

M. Benito and co-workers [22] have studied a new catalyst for hydrogen production by steam reforming of bio-ethanol. Three catalysts have been synthesized and tested for ethanol steam reforming. One of the developed catalysts was very active with 100% ethanol conversion at 700°C. Ethanol reforming over Ni/MgO and Ni/CeO₂ catalyst in molten carbonate fuel cell has been investigated by F. Frusteri *et al.* [23]. Both catalytic systems, at equilibrium conditions, are able to produce a rich hydrogen stream.

A global perspective of recent advances on the production and utilization trends of bio-fuels was referred by M. F. Demirbaş [24]. Hydrogen production by ethanol reforming over NiZnAl catalysts was studied by M. N. Barroso *et al.* [25]. They have obtained a complete ethanol conversion at 500 and 600°C. The product distribution depends on nickel loading the catalysts with Ni amounts between 18 and 25 wt.% which they are the ones showing the best performance [25].

Ceria-supported Co, Ir and Ni catalysts were investigated for steam reforming of ethanol in the temperature of 300°C - 700°C by B. Zhang *et al.* [26]. It was demonstrated that ceria supported catalyst were significantly active and selective for hydrogen production by steam reforming of ethanol. The strong interaction between Ir and CeO₂ effectively prevented the sintering and remarkably facilitated coke gasification [26]. L. Dolgykh *et al.* [27] studied the catalytic performance of Cu-containing industrial dehydrogenation catalyst for the steam reforming of ethanol using 12 wt% ethanol in water mixtures. The catalyst which was used in the study made achievement of hydrogen at 250°C - 300°C possible.

A. Akande *et al.* [28] studied kinetic modeling of hydrogen production by the catalytic reforming of crude ethanol over a Ni-Al₂O₃ catalyst in a packed bed tubular reactor. A few kinetic models was purposed. A power law model was also tried to fit the experimental data. Hydrogen production from ethanol reforming over alumina-supported nickel catalysts modified with Ce, Mg, Zr and La was studied by M. C. S. Sanchez *et al.* [29]. The activity of the catalysts was explained in terms of the different acidity, nickel dispersion or support-nickel interaction.

The effect of the morphology of nanocrystalline CeO₂ on ethanol reforming was studied by W. I. Hsiao *et al.* [30]. M. Ni *et al.* [31] carried out a research on reforming bio-ethanol for hydrogen production. They concluded that Ni and Rh based catalyst is the best choice for bio-ethanol conversion and hydrogen selectivity.

A review of bio-ethanol to produce hydrogen for a molten carbonate fuel cell was written by F. Frusteri and his co-worker [32]. This review demonstrated that the presence of low amount of oxygen in the reaction stream positively affects both activity and stability of catalyst.

A short communication about novel zeolite-supported rhodium catalyst for ethanol steam reforming was given by F. C. C. Skrobot *et al.* [33]. In conclusion, NaY zeolite-supported Rh has been suggested for ethanol-steam reforming. P. Biswas and D. Kunzru [34] studied catalytic steam reforming of ethanol both in presence and absence of oxygen over Ni-CeO₂-ZrO₂ catalyst. As a result, hydrogen yields were significantly affected by oxygen. In the absence of oxygen, higher hydrogen yield were obtained at higher temperatures.

Steam reforming of ethanol over Ni/support catalyst for generation of hydrogen was studied by A. Denis *et al.* [35]. It was found out that the most suitable supports in nickel catalysts designed for hydrogen generation in the steam reforming of ethanol are ZnO and TiO₂. Steam reforming of ethanol over an Ir/CeO₂ catalyst has been studied by B. Zhang *et al.* [36]. They have investigated the reaction mechanism and stability of the catalyst. They have concluded that the Ir/CeO₂ catalyst is significantly active for ethanol steam reforming and demonstrates good stability. Effect of Mg addition on ethanol steam reforming over Ni/Al₂O₃ catalysts was investigated by A. J. Vizcaino *et al.* [37]. The results demonstrated that Mg addition to Ni precursor leads to higher activities of prepared catalysts with an important reduction in the amount of deposited coke.

Hydrogen production through methanol steam reforming over Ni-Cu/CaO-SiO₂ catalysts activity was studied by Y. Ren-Xuan *et al.* [38] A modified polyol process conducted under an Ar atmosphere at 160°C can successfully synthesize Ni-Cu/CaO-SiO₂ catalysts, which are effective in SRM to produce H₂. Hydrogen production from n-butanol over alumina and modified alumina nickel catalysts was studied by K. Bizkarra *et al.* [39]. In that study modified supports and catalysts were prepared by wet impregnation method, and tested and compared with a commercial catalyst. They found some deactivation signs and between all tested catalysts the Ni/CeO₂-Al₂O₃ provided the highest hydrogen.

Thermodynamic and an experimental study of production of hydrogen from the steam and oxidative reforming of LPG was carried out by P. P. Silva *et al.* [40]. Their results showed that it is possible to produce high concentrations of hydrogen from LPG reforming. The gradual increase of temperature and the use of high water concentrations decrease the production of coke and increase the formation of H₂. Rh/Al₂O₃-La₂O₃ catalysts promoted with CeO₂ for ethanol steam reforming reaction was studied by P. Osorio-Vargasa *et al.* [41]. Rh-based catalysts supported on Al₂O₃-La₂O₃ modified with CeO₂ promoter were prepared. They reporting that catalyst exhibited good selectivity to H₂, with no presence of C₂ intermediates above 723°K. Reactivation tests showed that it is possible to recover part of the activity of the original catalyst after subjecting it to a pre-treatment by oxidation and reduction in order to remove any carbon deposits.

Syngas production from CO₂ reforming of methane over ceria supported cobalt catalyst and effects of reactants partial pressure was studied by B. V. Ayodele *et al.* [42]. The findings from this study show that syngas production from methane dry reforming over ceria-supported cobalt catalyst is significantly influenced by the variation in the partial pressure of the reactants. Their catalytic activity test shows that highest CO₂ and CH₄ conversions were obtained at CH₄ partial pressure of 45 and 25 kPa. Production of hydrogen from steam reforming of ethanol over LaNiO₃ and LaNiO₃/CeSiO₂ oxide types catalysts was studied by A. L. A. Marinhova *et al.* [43]. Their results showed that LaNiO₃/CeSiO₂ is a promising catalyst for H₂ production from ethanol, since their material exhibited high activity and lower carbon formation during SR of ethanol at 773°K. Hydrogen production by catalytic coal gasification and hydrogen production by ethanol steam reforming in two fixed bed reactors over eutectic salts (Li₂CO₃, Na₂CO₃ and K₂CO₃) and over a commercial BASF catalyst were studied by M. Levent *et al.* [44]-[48]. As a result, higher hydrogen ratios have been obtained at 5% - 10% eutectic salts and at lower ethanol/water ratios.

In this study, experimental studies were conducted under different temperatures, catalyst quantities and different state spaces over a commercial BASF catalyst and a laboratory prepared catalyst. In the case of commercial BASF catalyst hydrogen production rates were higher for similar experimental conditions of laboratory prepared catalyst. But, at temperatures over 700°C using commercial BASF catalyst for production of H₂ was not convenient, because H₂ production rates were reduced and some coke depositions were detected on the catalyst surfaces and deformation of catalyst was detected. In the case of using laboratory prepared catalyst up to 700°C, H₂ production rates were slightly lower (5% - 10%) than commercial catalyst. However, at temperatures over 700°C, better stabilities of laboratory catalyst have detected, and laboratory prepared catalyst were used for long periods and less carbon quantities are detected on the catalyst surfaces and H₂ production rates were slightly reduced over 700°C. At lower temperatures less than 700°C, using commercial catalyst has some advantages, but at temperatures higher than 700°C, using laboratory catalyst have some advantages about activity and stability. By carrying out some experiments at higher temperatures higher than 700°, some important achievements

and parameters were determined for industrial operation conditions of H_2 productions. At higher temperatures more than 700°C , some increments in production rate of CO were detected and a small decrement in H_2 rate and some decrements in CO_2 rate have been observed.

2. Experimental System

Experimental system was conducted in four sections (parts) (**Figure 1**): 1) Flow System: It contains 4 rotameters and each one has a 0 - 1000 ml/min of measurement capacity.

2) Steam system: It can be run in 0 - 4 bars operational pressure conditions; it has 0 - 6 ml/min water feeding capacity of one peristaltic pump which was made of nickel-chromia alloy steel. The steam system has a 1.5 m vertical pipe in length and it consists of connectors to reactor and pump, steam safety valve and one pressure gauge. Peristaltic pump is located in the bottom of the system. Water is pumped into the oven in reverse direction and it flows by evaporating into the reactor from top of the oven.

3) Reactor System: Two fixed bed reactors with higher temperature proof of chromia-nickel alloy, each one has 2 cm external, 1.5 cm internal diameters and each reactor has 93 cm and 83.5 cm in length, respectively [44]-[48]. Tubular oven has a cubic shape in external part and it is completely insulated against any temperature losses. The oven has a 5 cm internal diameter and 80 cm length. The ceramic pipe is completely rolled by a resistance wire material. This oven is covered with fire cement refracter. It can be heated up with 380 volts industrial electrical voltage and can be heated up to 1200°C temperature.

4) Gas analysis system is made up of two parts (units). A). Gas mixing system which is able to make up various gas mixtures. This system consists of 4 rotameters, each rotameter has a capacity of 0 - 1000 ml/min. Each of these rotameters is calibrated separately with pure H_2 , CH_4 , CO and CO_2 gases [38]-[42]. B). Midi GC (Model 1001 from Pherichrom company, Paris, France) gas analysis equipment has a 15 kg weight and a cubic shape equipment. There was a local control panel in front of the equipment. There was a TCD detector in the

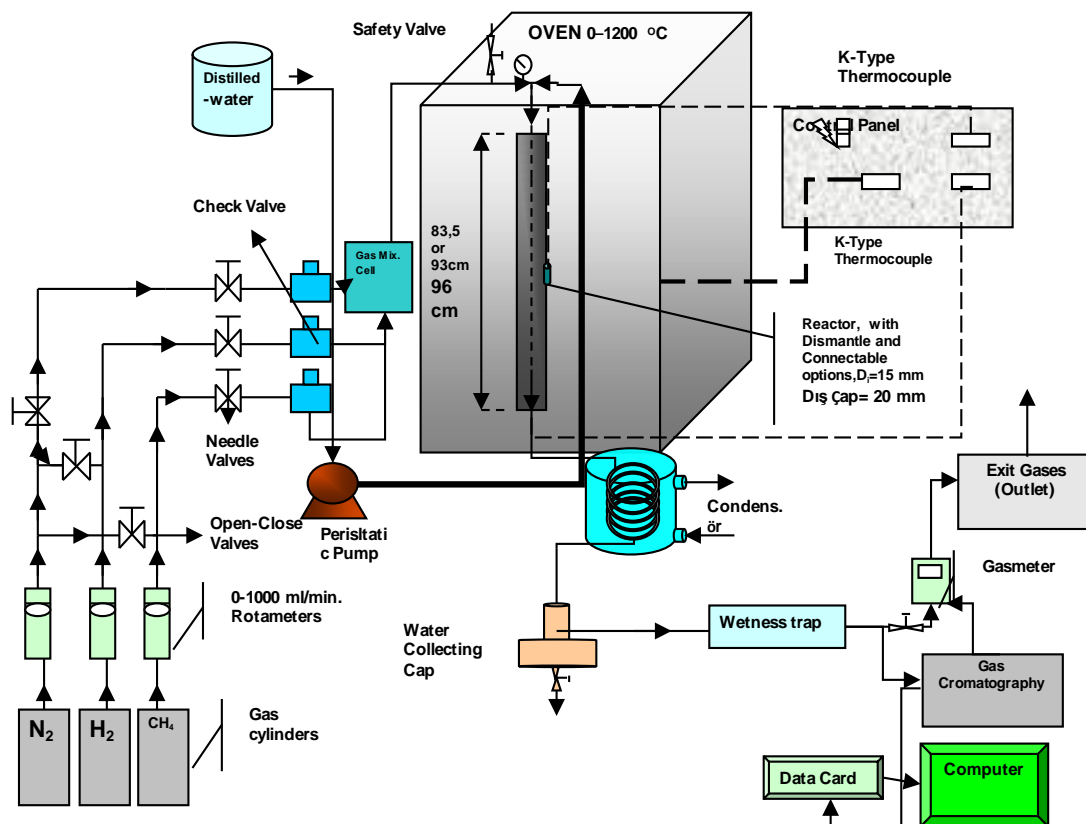


Figure 1. Flow diagram of experimental system (This experimental setup was designed by M. Levent for two completed projects (TÜBİTAK-MAG No: 106M162 and AÜ BAP No: 2004/101) [44]-[48]).

equipment. There were two packed columns in the equipment where one of them was porapak Q and the other one was molecular sieve column. The configuration of equipment was adjusted to do the analysis of exit gases in hydrocarbon reforming process. There are two automatic valves next to the equipment. One of the valve was commutation and the other one was the equilibrium valve [44]-[48].

Before starting to experimental studies, 1 - 5 grammes catalysts had been loaded into the reactor. In order to prevent any carbon deposition on catalyst surface, the catalyst had been conditioned at 500°C with 100 ml/min H₂ flow for 6 hours. Thus, NiO in the catalyst was reduced to metallic nickel. The activity of catalyst was provided [44]-[48].

At the beginning of the experiment, 200 ml/min N₂ gas was fed to the system. When system temperature reached to 250°C, nitrogen and hydrogen flows had been cutted off. In order to prevent catalyst surface from any coke formation, the conditioning experiments were carried out for designated intervals every day. The catalyst deformation related to the transmitted water droplets to the catalyst bed was prevented via heating the EtOH/water mixtures up to higher temperatures. After the reduction of the catalyst with H₂, in order to prevent the catalyst from any carbon deposition, the experiments were conducted continuously [44]-[48].

After the preparation of the catalyst for experiments, 0.5 - 1 ml/min EtOH/water mixtures were fed to the system. Temperature was raised gradually and in different temperatures the gas compositions were analyzed at the exit of the system. The system has a facility providing to analyse all the gases in the present study. Helium and nitrogen were used as carriers for GC. The exit voltages of GC analysis equipment were read continuously through an ADC card. The exit voltages were continuously observed in a monitor of Pentium-IV computer by the aid of a drawing program which was developed recently by Dizge analytical Co., Ankara, Turkey. All output peaks related to each experiment were stored in the computer. Then, peak areas of each gas in unknown samples were determined by GC and they were recorded in computer. By comparison of unknown samples peaks with pure gas samples, the composition of each component in unknown samples were determined [44]-[48].

The inlet pressure of carrier gas to GC was 2.1 bars and the temperature of GC oven was 80°C. While doing analysis with helium, detector current was 150 mA and accuracy was adjusted to 10. While analysing gas mixtures with nitrogen, detector current was adjusted to 60 mA and accuracy (gain) was adjusted as 10. GC accuracy balances were changed between 1 to 10. The value of 10 was the most accurate value of balance and 1 was the least accuracy value of gain (M. Levent, *et al.* [44]-[48]).

In the third stage of experimental programme, the oven resistance was replaced with a new resistance having a capacity of operating up to 700°C. Then, the rest of the experimental measurements were conducted at temperatures up to 700°C. Higher temperature operational conditions haven't been tried any more. All the remain experiments were carried out at temperatures between 250°C - 700°C and at catalyst loads of 1 to 5 grammes and at different ethanol/water ratios. As a result, through using lower ethanol/water ratios, higher hydrogen percentages were determined at the exit of the reactor system (see **Figures 2-9**).

2.1. The Composition of the Commercial BASF Catalyst and Catalyst Test Studies

In this study, the used commercial BASF catalyst was contained higher ratios of NiO. The catalyst has a 52% NiO, and other supports or promoters materials were SiO₂, MgO, CaO and Cr₂O₃. The catalyst has a cylindrical tablet shape with 3 mm height and 3 mm diameter. The catalyst density was 1006 kg/m³ and it can be used between 0 to 700°C operation temperatures. The specific surface area of catalyst was 247 m²/gr. Surface area measurement and trace element analysis of the catalyst were carried out with a BET equipment (Model: ASAP 2000), XRD and WDXRF equipments both at the beginning and at the final step of this study by taking permission from BASF company. In the initial step of tests, coke (carbon) couldn't be seen in the catalyst content. After one month study period, some carbon deposits were detected on the surface of the used catalyst. This is an indication demonstrating that a trace quantity of coke was formed on the catalyst surface during each experiment. But, the coke formation was very slow and the catalyst could only be used for one month. As a result, significant decline in hydrogen yields couldn't be observed in one month study period. In order to prevent the catalyst surface from any coke deposition, the reaction environment was kept in reductive conditions by providing a small stream of hydrogen through the reactor content.

2.2. The Composition of the Laboratory Prepared Catalyst and Catalyst Test Studies

In this study, a laboratory prepared catalyst which contains basically NiO, Al₂O₃ support and promoters such as

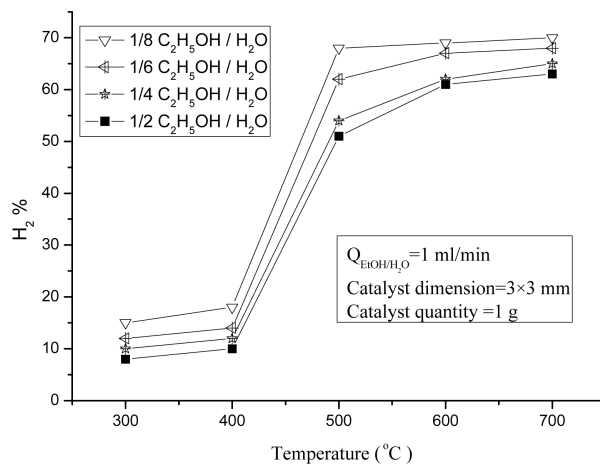


Figure 2. Reactor exit H_2 percentages for various EtOH/ H_2O ratios against temperature for commercial BASF catalyst [45] [47] [48].

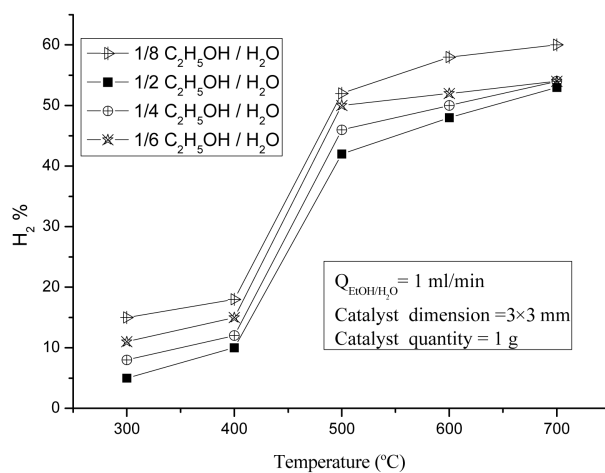


Figure 3. Reactor exit H_2 percentages for various EtOH/ H_2O ratios against temperature for commercial BASF catalyst [45] [47] [48].

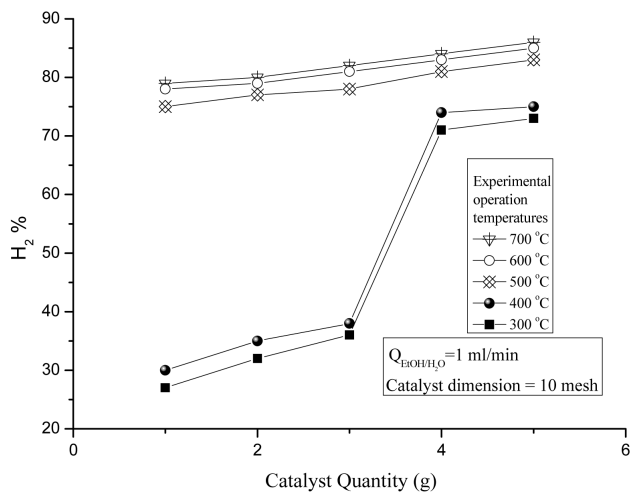


Figure 4. Reactor exit H_2 percentages for 1/8 EtOH/ H_2O value against commercial BASF catalyst quantity [45] [47] [48].

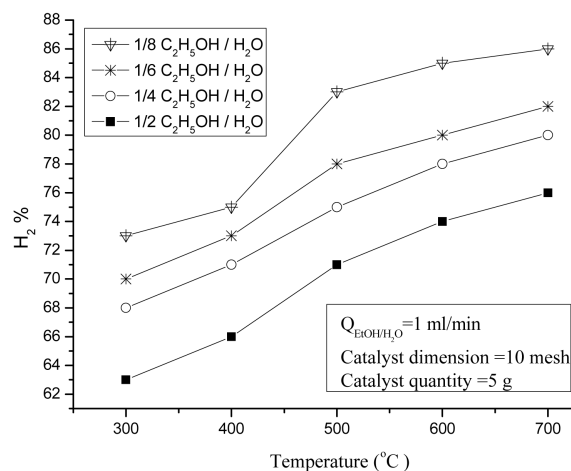


Figure 5. Exit H₂ percentages for various EtOH/H₂O ratios against temperature for commercial BASF catalyst [45] [47] [48].

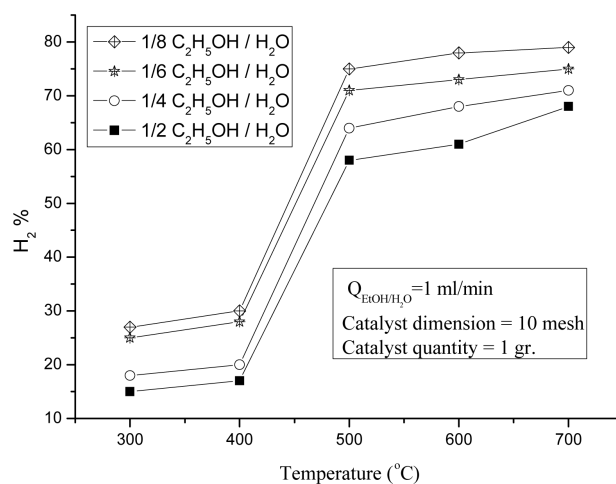


Figure 6. Exit H₂ percentages for various EtOH/H₂O ratios against temperature for commercial BASF catalyst.

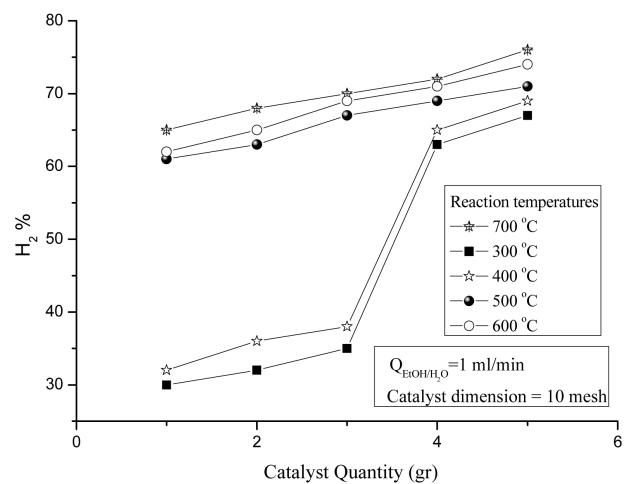


Figure 7. Exit H₂ percentages for 1/8 EtOH/H₂O value against laboratory prepared catalyst quantity [45] [47] [48].

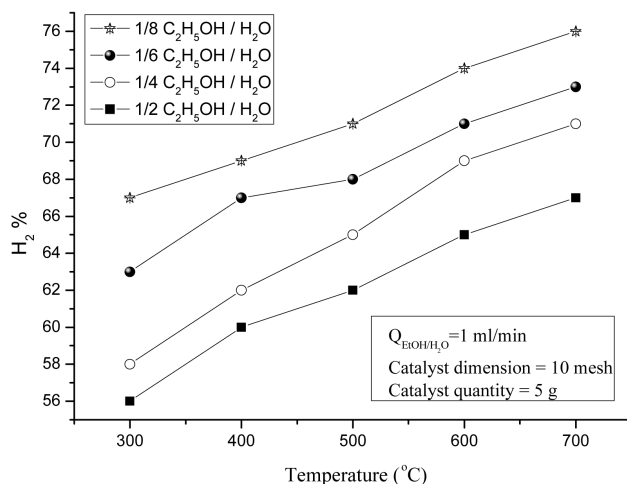


Figure 8. Exit H₂ percentages for various EtOH/H₂O ratios against temperature for laboratory prepared catalyst.

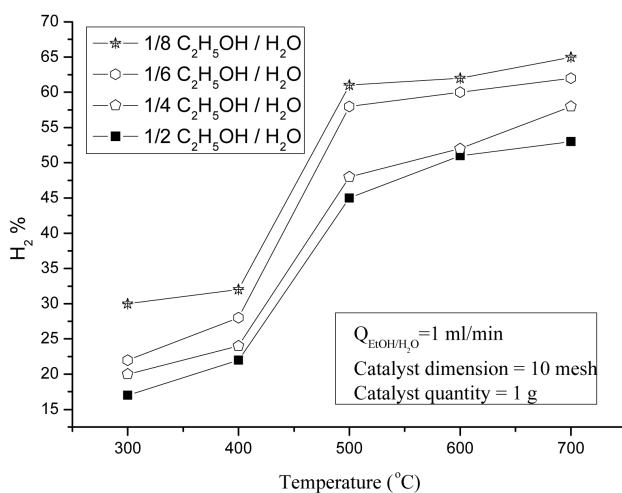


Figure 9. Exit H₂ percentages for various EtOH/H₂O ratios against temperature for laboratory prepared catalyst. [45] [47] [48].

SiO₂, MgO, CaO and Cr₂O₃ was synthesized. For this purpose, a weighed quantity of nickel nitrate (NiNO₃) salt was dissolved in distilled water. Then, it was added into a certain quantity of Al₂O₃ drop by drop. Then, it was stirred with a digital magnetic stirrer (Heidolph Mark, Model MR 3003 SD) and a digital mechanical stirrer (IKA Werk Mark, Model RE-166) at the speed of 300 rev./min. Simultaneously, other promoters (SiO₂, MgO, CaO and Cr₂O₃) were added into the same solution and it was stirred for an hour. In order to remove NO₃ deposits in calcination step without encountering any trouble, the pH of mixture was kept around 5,5 through adding an aqueous solution of NaOH drop by drop. The mixture of solution was filtered and dried in an oven. Then, it was calcined at 400°C. Then, the obtained catalyst powder was pelleted with a laboratory scale hydrolic press. The BET surface area of laboratory prepared catalyst was 115 m²/gr. SEM analysis of the laboratory prepared catalyst was also carried out. Then, catalyst pellets was used in the reactor. Some of the reaction runs were conducted with crushed catalyst particles (0.30 - 0.40 μm) of commercial BASF and laboratory prepared catalyst.

This laboratory prepared catalyst has a slightly less activity than commercial BASF catalyst. All reaction runs were carried on between 300°C to 700°C temperatures. As a result, the laboratory prepared catalyst has a longer life time than commercial BASF catalyst. Activity of commercial BASF catalyst was found slightly better than laboratory prepared catalyst.

3. Results and Discussions

In this study, hydrogen production yields were investigated at different EtOH/water ratios and at different temperatures with ethanol-water vapour process over a commercial BASF and a laboratory prepared catalyst. In this experimental study based on volume ratios of 1/10, 1/8, 1/6, 1/4 and 1/2, ethyl alcohol/water ratios at different temperatures (300, 400, 500, 600, 700°C) obtained peak areas of hydrogen and produced H₂ % values have been computed.

A new catalyst (NiO/Al₂O₃) promoted by CaO, MgO and Cr₂O₃ was prepared and it was used for H₂ production under similar experimental conditions of commercial BASF catalyst. The laboratory prepared catalyst has demonstrated higher activity values (upto 70% H₂ values). And longer catalyst life time was observed during ethanol-steam reforming reaction. The hydrogen yields in the exit gas composition increased slightly in parallel with the increase of catalyst loads. The hydrogen yields in exit gas composition also increased with the increase in temperature and decrease in EtOH/water ratios. The duration of laboratory prepared catalyst is longer (2 - 3 weeks) than the duration of commercial BASF catalyst (1 - 2 weeks). The maximum operation temperature of commercial BASF catalyst was 700°C. However, the laboratory prepared catalyst has been used at higher temperatures (800°C - 900°C). In the first stage of the study, some experiments were carried out at higher temperatures above 700°C. The laboratory prepared catalyst has demonstrated good activity levels even at higher temperatures over 700°C. But, the oven resistance was burned out at higher temperature operations.

Reaction started around 300°C and the reaction rate was increasing proportionally with the temperature. Hydrogen yields were slightly increasing in parallel with the increases in catalyst loads. At very high temperatures over 700°C up to 900°C, the sintering and coke deposition in commercial BASF catalyst was slightly higher than laboratory prepared catalyst. The activity of laboratory prepared catalyst was longer than commercial BASF catalyst. But the hydrogen yields and activity of commercial BASF catalyst was slightly higher than laboratory prepared catalyst at operational temperatures up to 700°C. The coke deposition rates in both catalyst surfaces were increasing with higher ethanol/water ratios of feed. Coke deposition on catalyst surface during 1/2 volume ratio of ethanol/water feed was higher than coke deposition during 1/10 volume ratio of EtOH/H₂O feed.

H₂ percentages against temperature for 1/10 EtOH/water ratio was given in **Figure 2**. As it can be seen on **Figure 2**, H₂ percentages have demonstrated a rapid increase to over 80% at 300°C. This indicated that EtOH/H₂O reaction over BASF commercial catalyst was taken place rapidly at 300°C to higher temperatures. Exit H₂ percentages against temperatures at different EtOH/H₂O ratios over 1 gr. of commercial BASF catalyst were given on **Figure 2**. As it can be seen on graph, the percentages of H₂ were varied between 7% to 15% at 300°C and at different EtOH/H₂O ratios between 1/2 - 1/8 when temperature values increased from 400 to 500°C, and H₂ percentages were increased, sharply from a range of 7% - 15% to a range of 50% - 70%. If EtOH/H₂O ratios were declined from 1/2 to 1/8 at 700°C, then, H₂ percentages were changed to a range of 60% - 70% at the exit of the reactor. As a result, H₂ percentages are linearly proportional with increments in temperatures and decrements in EtOH/H₂O ratios between 1/2 - 1/8 and H₂ percentages were inversely proportional with decrements in temperature from 700°C to 300°C.

Exit H₂ percentages which are ranged from 4% to 60% over 1 gram of laboratory prepared catalyst were given on **Figure 3**. As it can be seen on this figure, H₂ percentages increased slightly from 5% to 17% at lower temperatures from 300°C to 400°C. When temperature was increased from 400°C to 500°C, H₂ percentages increased sharply from the range of 5% - 17% to the range of 40% - 53%. If temperature was increased further from 500°C to 700°C, H₂ percentages also slightly increased to the range of 50% - 60%. As a result, H₂ percentages increased in the parallel with temperatures, and EtOH/H₂O ratios are effective on H₂ yields.

Exit H₂ percentages for 1/8 EtOH/H₂O ratios against quantities of commercial BASF catalyst were given in **Figure 4**. As seen on this graph, when the quantities of commercial BASF catalyst were increased from 0 to 5 grammes, hydrogen percentages in exit gas composition also increased linearly. H₂ percentages were found around 66% - 70% in the temperature ranged from 500 to 700°C. However, in the temperature range of 300°C - 400°C with lower catalyst quantities from 1 to 3 grammes, H₂ percentages increased slightly from 25% to 35%. When catalyst loads were increased from 3 to 4 grammes, H₂ percentages increased sharply to the range of 70% - 72%. When catalyst quantities were increased from 4 to 5 grammes, H₂ percentages increased slightly to the range of 70% - 73%. As a result, H₂ percentages depend on temperature increments and H₂ percentages are increasing with quantities of commercial BASF catalyst.

Exit H_2 percentages against different temperatures for commercial BASF catalyst were given in **Figure 5**. As seen on this graph, H_2 percentages increase linearly with temperature. While produced H_2 percentages are higher at lower EtOH/ H_2O ratios, produced H_2 percentages are lower at higher ethanol/water ratios. H_2 percentages changed in the range of 63% - 73% at 300°C. When temperature was increased to 700°C, the range of H_2 percentage became 72% - 85%. In the lights of these findings it can be said that H_2 percentages increase in the exit of the reactor parallel with temperature increments in reactor system.

H_2 percentages against temperatures over 1 gram of commercial BASF catalyst were given in **Figure 6**. H_2 percentages were increased in three steps. In first step (300 to 400°C), H_2 percentages were increased slightly. In second step (400 to 500°C), H_2 percentages were increased sharply and in final step (500 to 700°C), H_2 percentages were increased slightly to the range of 65% - 80%.

Exit H_2 percentages against laboratory prepared catalyst quantities were given in **Figure 7**. As seen on this graph developed for 1/8 EtOH/ H_2O ratio, when catalyst quantities were increased from 1 to 5 grammes, H_2 percentages also increased from lower values to higher values. For the catalyst range from 1 to 3 grammes and temperature range of 300°C - 400°C, H_2 percentages changed from the range of 29% - 32%, to the range of 33% - 35%. When catalyst loads were increased from 3 grammes to 4 grammes at same temperature range, H_2 percentages increased sharply to the range of 58% - 60%. For further increments in catalyst loads at the same temperature range, H_2 percentages were increased, slightly to a range of 63% - 65%. For temperature range of 500°C to 700°C with increments in catalyst loads from 1 to 5 grammes, linear increments in H_2 percentages were achieved in the range of 60% - 65% and 65% - 75%.

Exit H_2 percentages at different temperatures and different ethanol/water ratios over 5 grammes of laboratory prepared catalyst were given in **Figure 8**. As it can be seen on this figure, H_2 percentages at 300°C linearly increased from the range of 56% - 67% to the range of 66% - 75% at 700°C. Exit H_2 percentages at different temperatures and different EtOH/ H_2O ratios were given on **Figure 9**. In this figure H_2 percentages were also increased in three steps. In first stage whose temperature ranged from 300 to 400°C, H_2 percentages increased slightly from the range of 17% - 30% to a range of 18% - 32%. In second stage whose temperature ranged between 400 to 500°C, H_2 percentages increased sharply from the range of 20% - 30% to the range of 43% - 60%. At further temperatures from 500 to 700°C, H_2 percentages increased slightly to the range of 50% - 63% at 700°C.

Peak areas at different temperatures for 1 gram of commercial BASF catalyst and 1/8 EtOH/ H_2O ratio were given in **Figure 10**. Peak areas of H_2 were linearly increased from 500 millivolts(mVs) at 300°C to 4000 mVs at 500°C. While peak areas of H_2 were increased slightly to the value of 4300 mVs at 700°C, The peak areas of other gases were changed between 100 to 800 mVs at temperature range of 300 to 700°C.

Peak areas at different temperatures for 1 gram of laboratory prepared catalyst and 1/8 EtOH/ H_2O ratio were given on **Figure 11**. In this graph, it can be seen that peak areas of H_2 were continuously increased from 0 mVs to 3000 mVs with increasing temperature. Peak areas of H_2 were increased linearly to a value of 3800 mVs,

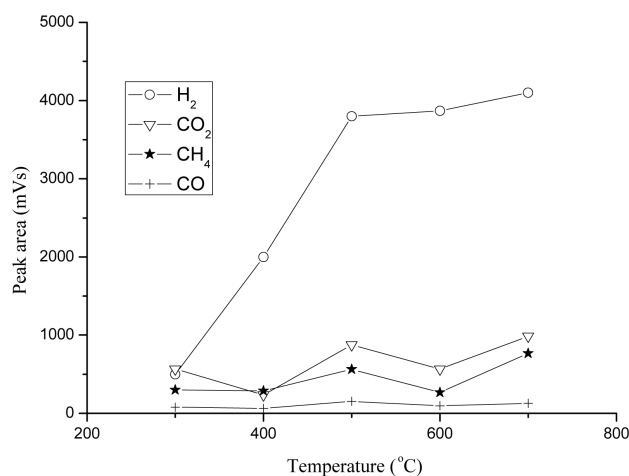


Figure 10. Pick areas of all exit gases for 1 gramme commercial BASF catalyst and 1/8 EtOH/ H_2O value.

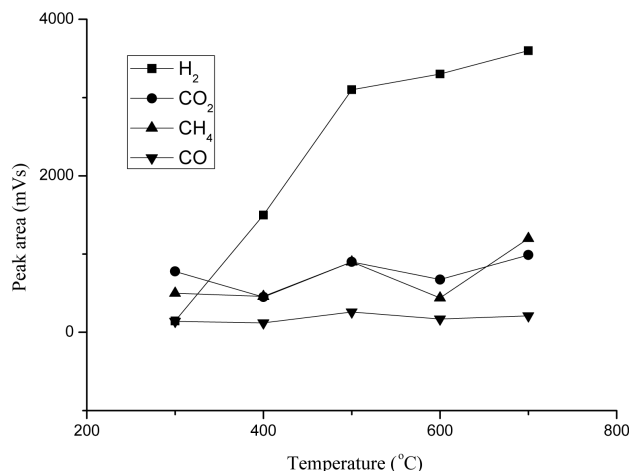


Figure 11. Pick areas of all exit gases for 1 gramme of laboratory prepared catalyst and 1/8 EtOH/H₂O value [45] [47] [48].

approximately at 700°C. Peak areas of other gases (CO₂, CH₄, CO) are changed in the range of 50 - 1000 mVs, approximately.

Ethanol conversion percentages at different Space times (W/F_{A0}) and at different temperatures (500°C - 700°C) for 1/8 EtOH/H₂O ratio over commercial BASF catalyst were given in Figure 12. As it can be seen on this graph, ethanol conversions also increase parabolically at temperatures 500°C and 600°C with increment in space times. However, H₂ percentages increase linearly with increment in space times at temperature of 700°C.

Higher ethanol conversion values (in the range of 85% - 100%) at different spaces times (in the range of 0.015 - 0.060) and at 700°C were achieved. At different spaces times (in the range of 0.015 - 0.060) and at different temperatures (500°C and 600°C), different ethanol conversion ranges of 86% - 88% and 92% - 93% were achieved, respectively.

Ethanol conversions at different space times (W/F_{A0}) and at different temperatures for 1/8 EtOH/H₂O ratio and laboratory prepared catalyst were given on Figure 13. As seen on this graph, ethanol conversion increase with increments in space times.

At higher temperatures (700°C), 98% of ethanol conversion was achieved over laboratory prepared catalyst. Ethanol conversions at different temperatures increase with space times (W/F_{A0}). Peak areas (mVs) of all gases at different space times (W/F_{A0}) for 1/8 EtOH/H₂O ratio over commercial BASF catalyst were given on Figure 14. As seen on this graph, peak areas of H₂ is higher than peak areas of other gases (CO₂, CH₄, CO). Peak areas of H₂ were changed between 4000 mVs and 5000 mVs. The peak areas of other gases were changed between 50 mVs and 1000 mVs.

Peak areas of all gases at different space times (W/F_{A0}) for 1/8 EtOH/H₂O ratio over laboratory prepared catalyst were given on Figure 15. As seen on graph, peak area of H₂ is higher than peak areas of other gases (CO₂, CH₄, CO). Peak areas of H₂ were changed in the range of 3800 - 4200 mVs. However, peak areas of other gases were changed in the range of 100 mVs - 1100 mVs.

The reaction kinetic parameters can be calculated on the basis of the following equations. The derivation of the differential and integral forms of the design equations for packed bed reactors were given by H.S. Fogler [43]:

$$-R'_{EtOH} = \frac{F_{EtOH}^0 \cdot dX}{dW} = \frac{P_{EtOH}}{R \cdot T} \cdot \frac{dX_{EtOH}}{dW} \quad \text{and} \quad W = F_{EtOH}^0 \int_0^X \frac{dX_{EtOH}}{dW} \quad (5)$$

where F_{EtOH}^0 is molar flowrate of ethanol, P_{EtOH} is partial pressure of ethanol, R is gas constant, W is Catalyst weight, T is absolute temperature and X is mole fraction of each component. The activation energy is determined experimentally by carrying out the reaction at several different temperatures [43]:

$$-R'_{EtOH} = k \cdot C_{EtOH} = k \cdot \frac{P_{EtOH}}{R \cdot T} \quad \text{and} \quad k = A \cdot e^{\frac{-E_A}{R \cdot T}} \quad (6)$$

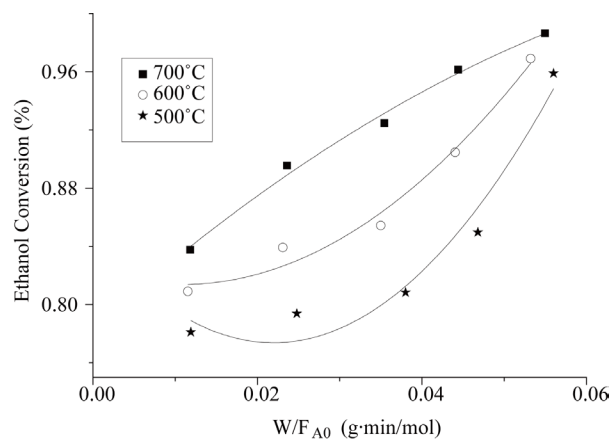


Figure 12. Ethanol conversion against space time in the reactor with different gas temperatures from obtained data at 1/8 EtOH/H₂O ratio with commercial BASF catalyst [45] [47] [48].

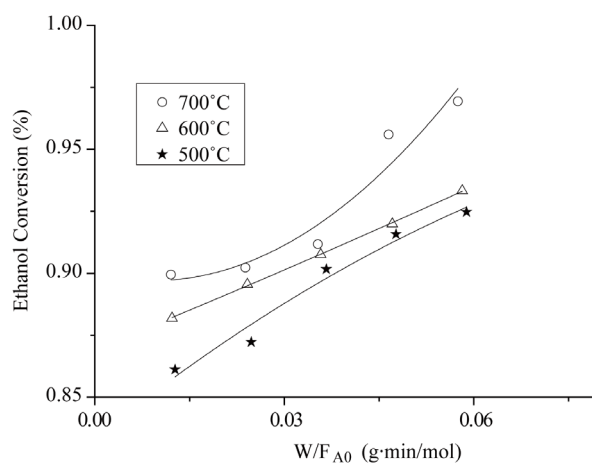


Figure 13. Ethanol conversion against space time in the reactor with different gas temperatures from obtained data at 1/8 EtOH/H₂O ratio with laboratory prepared catalyst [45] [47] [48].

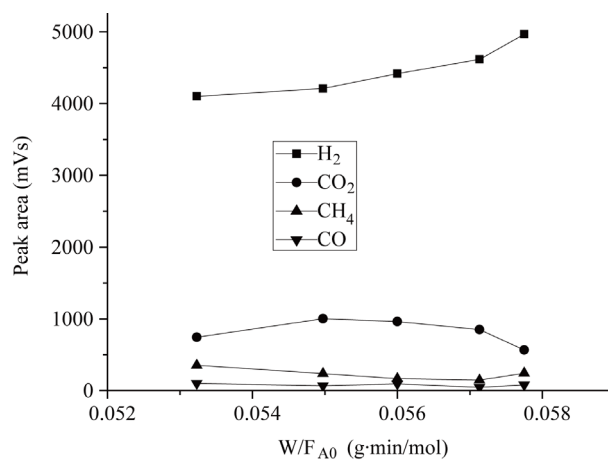


Figure 14. Pick areas of all gases obtained at the exit of the reactor against space time in the reactor of gases from obtained data in 1/8 EtOH/H₂O ratio with commercial BASF catalyst [45] [47] [48].

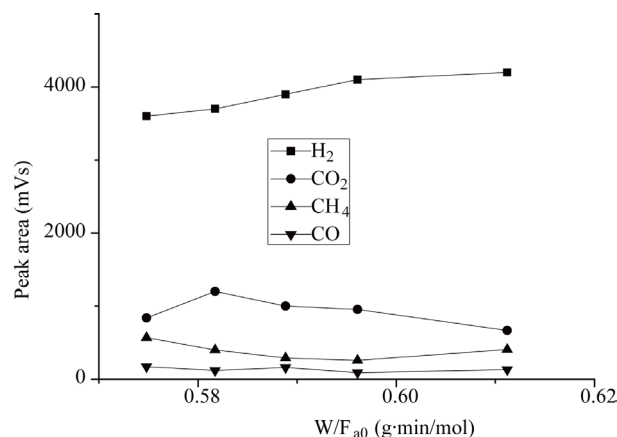


Figure 15. Peak areas of all gases obtained at the exit of the reactor against space time in the reactor from obtained data of gases at the 1/8 EtOH/H₂O ratio with laboratory prepared catalyst [45] [47] [48].

where k is reaction rate constant, A is frequency factor, E_A is activation energy and T is absolute temperature. In order to calculate the activation energies and determine the diffusion effects on the reaction rates, $\ln k$ graph against inverse of absolute temperatures for 1/8 ratio of EtOH/H₂O ratio over 5 grammes of commercial BASF catalyst were given in Figure 16. As seen on this graph, $\ln k$ values are inversely linear with the reverse of absolute temperatures. Diffusion effects on overall reaction rate may not be very significant. But, some indications of diffusion were determined during computation of activation energies. Because, different activation energy values were obtained over different catalyst quantities. When loaded catalyst quantities were increased, the determined activation energy values were also increased significantly.

In order to calculate the activation energies and understand the diffusion effects on overall reaction rate, $\ln k$ graph against inverse of absolute temperatures for 1/8 EtOH/H₂O ratio and 5 grammes of laboratory prepared catalyst was drawn on Figure 17.

As seen on graph, $\ln k$ values are inversely linear with the inverse of absolute temperatures. This means that diffusion effects related to the reaction are small and the reaction may be taken as first order. From the slope of this graph, the activation energy of ethanol-steam reforming reaction could be determined. The activation energies of different experimental runs were also calculated from Arrhenius equation [49]. Activation energy values determined from theoretical equations and activation energies determined from graphs were found in good agreement in the range of 6.50 to 52.7 kJ/moles. Determined activation energies strongly depend on the type and quantities of the treated catalyst.

4. Conclusions

So far, some kinetic parameters related to ethanol-steam reforming reaction were determined at different temperature conditions and at different catalyst loads with different ethanol/water feed ratios. On the basis of obtained kinetic parameters, ethanol-steam reforming reaction was put in the first order and chemical reaction was controlled. The obtained activation energies have good fit with similar studies in literature [50]-[52]. As a result of experiments conducted at different ethanol/water ratios, at different temperatures and at different catalyst loads (1 to 5 grammes), H₂ yields were computed. In the exit gas compositions, the highest hydrogen concentrations were found at lower EtOH/water feed ratios and at higher temperatures. Experimental work was completed by using different catalyst dimensions in parallel with different catalyst loads and different ethanol/water feed ratios at different times.

Two series of experimental measurements were carried out in this study. First series of experimental measurements is performed over a commercial BASF catalyst which is perfect up to temperatures of 700°C. The second series of experimental measurements are carried out with a laboratory prepared catalyst at temperatures up to 900°C. Hydrogen production rates over commercial BASF catalyst are slightly higher (5% - 10%) than hydrogen production rates over laboratory prepared catalyst up to temperatures of 700°C. But, hydrogen production rates over laboratory prepared catalyst were found slightly higher (5%) than commercial BASF catalyst

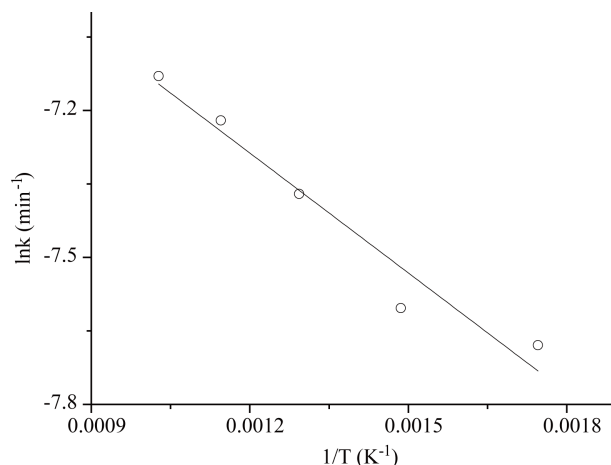


Figure 16. Graph of $\ln k$ against $1/T$ from obtained data at the 1/8 EtOH/H₂O ratio with 5 grammes of commercial BASF catalyst [48].

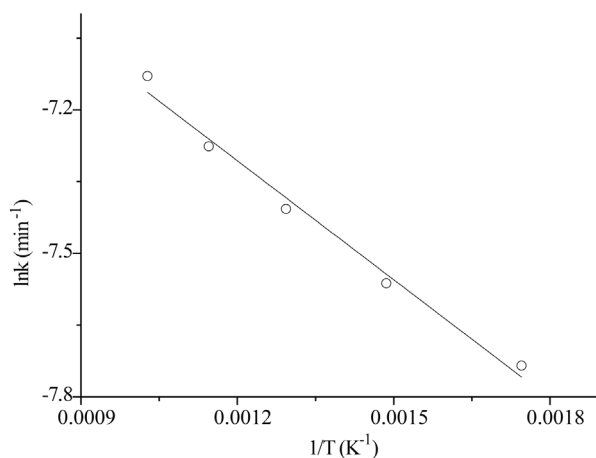


Figure 17. $\ln k$ graph against $1/T$ from obtained data at the 1/8 EtOH/H₂O ratio with 5 grammes of laboratory prepared catalyst [48].

at temperatures between 700°C - 900°C and activity of laboratory prepared catalyst is better than activity of commercial BASF catalyst at temperatures above 700°C. Because, differences in hydrogen production rates were less even at temperatures above 700°C for a duration of 2 weeks. But, differences in hydrogen production rates were higher (10% - 15%) over commercial BASF catalyst above 700°C. This means that activity of commercial BASF catalyst was reducing at temperatures above 700°C.

In this study, it can be seen that overall reaction is an endothermic reaction. The lower values of activation energies demonstrate that diffusion resistance has not an important effect on reaction rate. Catalyst loads were kept lower (1 to 5 grammes) in order to provide isothermal temperature distribution in the reactor content. Thus, measurements of intrinsic reaction kinetic were purposed. Experimental studies with different catalyst dimensions and different time on steams (0 - 240 minutes) were conducted at the temperature range of 250°C - 700°C and different ethanol/water ratios. The activation energy values of reaction were in the range of 6.504 kJ/mole to 52.717 kJ/mole, and the average value of activation energy was calculated as 26.870 kJ/mole. The reaction was controlled by chemical reaction, but in the case of higher activation energies, some diffusion resistances were taken place in the catalyst bed. The obtained activation energy values which are identical with the activation energies with similar catalyst contents have been presented in literature [50]-[52]. The sintering ratio of commercial BASF catalyst was found higher at operational temperatures over 700°C than sintering ratio of laboratory prepared catalyst at similar operational conditions. The optimum life time on stream of commercial BASF catalyst was found as one week, and the optimum life time on stream of laboratory prepared catalyst was found

as 2 weeks at operational temperatures up to 900°C.

As a result of experimental measurements and some calculations, we have found that by reducing ethanol ratios in the water is resulting higher hydrogen production rates at the exit of reactors. In the case of higher ethanol/water ratios in the entrance of the reactor, lower hydrogen yields were detected at the exit of the reactors. In the case of higher ethanol/water ratios in the feed, higher coke formation rates have obtained on the surface of the catalyst. Therefore, lower ethanol/water ratios were preferred during this experimental study, and so, higher hydrogen production rates had determined at the exit of the experimental system. We are planning to do some further experimental measurements related to this study over various catalyst contaminations at a temperature range of 200°C - 900°C. By performing such an experimental programme, more valuable data will be produced for industrial hydrogen productions.

Acknowledgements

Authors wish to thank Chemical Engineering Department of Atatürk University, for the given opportunity to work in their Laboratory during experimental measurements. Authors also thanks to Turkish Scientific Research Council (TÜBİTAK) and Atatürk University for financial supports during project studies.

References

- [1] Marino, F.J., Cerrella, E.G., Duhalde, S., Jobbagy, M. and Laborde, M.A. (1998) Hydrogen from Steam Reforming of Ethanol, Characterization and Performance of Copper-Nickel Supported Catalysts. *International Journal of Hydrogen Energy*, **23**, 1095-1101. [http://dx.doi.org/10.1016/S0360-3199\(97\)00173-0](http://dx.doi.org/10.1016/S0360-3199(97)00173-0)
- [2] Fishtik, I., Alexander, A., Datta, R. and Geana, D. (2000) A Thermodynamics Analysis of Hydrogen Production by Steam Reforming of Ethanol via Response Reactions. *International Journal of Hydrogen Energy*, **25**, 31-45. [http://dx.doi.org/10.1016/S0360-3199\(99\)00004-X](http://dx.doi.org/10.1016/S0360-3199(99)00004-X)
- [3] Galvita, V.V., Semin, G.L., Belyaev, V.D., Semikolenov, V.A., Tsiakaras, P. and Sobyenin, V.A. (2001) Synthesis Gas Production by Steam Reforming of Ethanol. *Applied Catalysis A: General*, **220**, 123-127. [http://dx.doi.org/10.1016/S0926-860X\(01\)00708-6](http://dx.doi.org/10.1016/S0926-860X(01)00708-6)
- [4] Therdthianwong, A., Sakulkoakiet, T. and Therdthianwong, S. (2001) Hydrogen Production by Catalytic Ethanol Steam Reforming. *Science Asia*, **27**, 193-198. <http://dx.doi.org/10.2306/scienceasia1513-1874.2001.27.193>
- [5] Lindström, B. (2001) Hydrogen Generation by Steam Reforming of Methanol over Copper-Based Catalysts for Fuel Cell Applications. *International Journal of Hydrogen Energy*, **26**, 923-933. [http://dx.doi.org/10.1016/S0360-3199\(01\)00034-9](http://dx.doi.org/10.1016/S0360-3199(01)00034-9)
- [6] Klouz, V., Fierro, V., Denton, P., Katz, H., Lisse, J.P., Bouvot-Mauduit, S. and Mirodatos, C. (2002) Ethanol Reforming for Hydrogen Production in a Hybrid Electric Vehicle: Process Optimization. *Journal of Power Sources*, **105**, 26-34. [http://dx.doi.org/10.1016/S0378-7753\(01\)00922-3](http://dx.doi.org/10.1016/S0378-7753(01)00922-3)
- [7] Freni, S., Cavallaro, S., Mondello, N., Spadaro, L. and Frusteri, F. (2002) Steam Reforming of Ethanol on Ni/MgO Catalysts: H₂ Production for MCFC. *Journal of Power Sources*, **108**, 53-57. [http://dx.doi.org/10.1016/S0378-7753\(02\)00004-6](http://dx.doi.org/10.1016/S0378-7753(02)00004-6)
- [8] Joensen, F. and Rostrup-Nielsen, J.R. (2002) Conversion of Hydrocarbons and Alcohols for Fuel Cells. *Journal of Power Sources*, **105**, 195-201. [http://dx.doi.org/10.1016/S0378-7753\(01\)00939-9](http://dx.doi.org/10.1016/S0378-7753(01)00939-9)
- [9] Fatsikostas, A.N., Kondarides, D.I. and Verykios, X.E. (2002) Production of Hydrogen for Fuel Cells by Reformation of Biomass-Derived Ethanol. *Catalysis Today*, **75**, 145-155. [http://dx.doi.org/10.1016/S0920-5861\(02\)00057-3](http://dx.doi.org/10.1016/S0920-5861(02)00057-3)
- [10] Cavallaro, S., Chiodo, V., Vita, A. and Freni, S. (2003) Hydrogen Production by Auto-Thermal Reforming of Ethanol on Rh/Al₂O₃ Catalyst. *Journal of Power Sources*, **123**, 10-16. [http://dx.doi.org/10.1016/S0378-7753\(03\)00437-3](http://dx.doi.org/10.1016/S0378-7753(03)00437-3)
- [11] Liguras, D.K., Kondarides, D.I. and Verykios, X.E. (2003) Production of Hydrogen for Fuel Cells by Steam Reforming of Ethanol over Supported Noble Metal Catalysts. *Applied Catalysis B: Environmental*, **43**, 345-354. [http://dx.doi.org/10.1016/S0926-3373\(02\)00327-2](http://dx.doi.org/10.1016/S0926-3373(02)00327-2)
- [12] Marino, F., Baronetti, G., Jobbagy, M. and Laborde, M. (2003) Cu-Ni-K/ γ -Al₂O₃ Supported Catalysts for Ethanol Steam Reforming Formation of Hydrotalcite-Type Compounds as a Result of Metal-Support Interaction. *Applied Catalysis A: General*, **238**, 41-54. [http://dx.doi.org/10.1016/S0926-860X\(02\)00113-8](http://dx.doi.org/10.1016/S0926-860X(02)00113-8)
- [13] Cavallaro, S., Chiodo, V., Freni, S., Mondello, N. and Frusteri, F. (2003) Performance of Rh/Al₂O₃ Catalyst in the Steam Reforming of Ethanol: H₂ Production for MCFC. *Applied Catalysis A: General*, **249**, 119-128. [http://dx.doi.org/10.1016/S0926-860X\(03\)00189-3](http://dx.doi.org/10.1016/S0926-860X(03)00189-3)
- [14] Comas, J., Marino, F., Laborde, M. and Amadeo, N. (2004) Bio-Ethanol Steam Reforming on Ni/ Al₂O₃ Catalyst.

- Chemical Engineering Journal*, **98**, 61-68. [http://dx.doi.org/10.1016/S1385-8947\(03\)00186-4](http://dx.doi.org/10.1016/S1385-8947(03)00186-4)
- [15] Frusteri, F., Freni, S., Chiodo, V., Spadaro, L., Di Blasi, O., Bonura, G. and Cavallaro, S. (2004) Steam Reforming of Bio-Ethanol on Alkali-Doped Ni/MgO Catalysts: Hydrogen Production for MC Fuel Cell. *Applied Catalysis A: General*, **270**, 1-7. <http://dx.doi.org/10.1016/j.apcata.2004.03.052>
 - [16] Akande, A.J., Idem, R.O. and Dalai, A.K. (2005) Synthesis, Characterization and Performance Evaluation of Ni/Al₂O₃ Catalysts for Reforming of Crude Ethanol for Hydrogen Production. *Applied Catalysis A: General*, **287**, 159-175. <http://dx.doi.org/10.1016/j.apcata.2005.03.046>
 - [17] Vesselli, E., Comelli, G., Rosei, R., Freni, S., Frusteri, F. and Cavallaro, S. (2005) Ethanol Auto-Thermal Reforming on Rhodium Catalysts and Initial Steps Simulation on Single Crystals under UHV Conditions. *Applied Catalysis A: General*, **281**, 139-147. <http://dx.doi.org/10.1016/j.apcata.2004.11.020>
 - [18] Lisboa, J.S., Santos, D.C.R.M., Passos, F.B. and Noronha, F.B. (2005) Influence of the Addition of Promoters to Steam Reforming Catalysts. *Catalysis Today*, **101**, 15-21. <http://dx.doi.org/10.1016/j.cattod.2004.12.005>
 - [19] Velu, S., Suzuki, K., Vijayaraj, M., Barman, S. and Gopinath, C.S. (2005) *In Situ* XPS Investigations of Cu_{1-x}Ni_xZnAl-Mixed Metal Oxide Catalysts Used in the Oxidative Steam Reforming of Bio-Ethanol. *Applied Catalysis B: Environmental*, **55**, 287-299. <http://dx.doi.org/10.1016/j.apcatb.2004.09.007>
 - [20] Aupretre, F., Descorme, C., Duprez, D., Casanave, D. and Uzio, D. (2005) Ethanol Steam Reforming over Mg_xNi_{1-x}Al₂O₃ Spinel Oxide-Supported Rh Catalysts. *Journal of Catalysis*, **233**, 464-477. <http://dx.doi.org/10.1016/j.jcat.2005.05.007>
 - [21] Mattos, L.V. and Noronha, F.B. (2005) The Influence of the Nature of the Metal on the Performance of Cerium Oxide Supported Catalysts in the Partial Oxidation of Ethanol. *Journal of Power Source*, **152**, 50-59. <http://dx.doi.org/10.1016/j.jpowsour.2004.12.052>
 - [22] Benito, M., Sanz, J.L., Isabel, R., Padilla, R., Arjona, R. and Daza, L. (2005) Bio-Ethanol Steam Reforming: Insights on the Mechanism for Hydrogen Production. *Journal of Power Sources*, **151**, 11-17. <http://dx.doi.org/10.1016/j.jpowsour.2005.02.046>
 - [23] Frusteri, F., Freni, S., Chiodo, V., Donato, S., Bonura, G. and Cavallaro, S. (2006) Steam and Auto-Thermal Reforming of Bio-Ethanol over MgO and CeO₂ Ni Supported Catalysts. *International Journal of Hydrogen Energy*, **31**, 2193-2199. <http://dx.doi.org/10.1016/j.ijhydene.2006.02.024>
 - [24] Demirbas, M.F. and Balat, M. (2006) Recent Advances on the Production and Utilization Trends of Bio-Fuels: A Global Perspective. *Energy Conversion and Management*, **47**, 2371-2381. <http://dx.doi.org/10.1016/j.enconman.2005.11.014>
 - [25] Barroso, M.N., Gomez, M.F., Arrua, L.A. and Abello, M.C. (2006) Hydrogen Production by Ethanol Reforming over NiZnAl Catalysts. *Applied Catalysis A: General*, **304**, 116-123. <http://dx.doi.org/10.1016/j.apcata.2006.02.033>
 - [26] Zhang, B., Tang, X., Li, Y., Cai, W., Xu, Y. and Shen, W. (2006) Steam Reforming of Bio-Ethanol for the Production of Hydrogen over Ceria-Supported Co, Ir and Ni Catalysts. *Catalysis Communications*, **7**, 367-372. <http://dx.doi.org/10.1016/j.catcom.2005.12.014>
 - [27] Dolgikh, L., Stolyarchuk, I., Deynega, I. and Strizhak, P. (2006) The Use of Industrial Dehydrogenation Catalysts for Hydrogen Production from Bioethanol. *International Journal of Hydrogen Energy*, **31**, 1607-1610. <http://dx.doi.org/10.1016/j.ijhydene.2006.06.028>
 - [28] Akande, A., Aboudheir, A., Idem, R. and Dalai, A. (2006) Kinetic Modeling of Hydrogen Production by the Catalytic Reforming of Crude Ethanol over a Co-Precipitated Ni-Al₂O₃ Catalyst in a Packed Bed Tubular Reactor. *International Journal of Hydrogen Energy*, **31**, 1707-1715. <http://dx.doi.org/10.1016/j.ijhydene.2006.01.001>
 - [29] Sanchez-Sanchez, M.C., Navarro, R.M. and Fierro, J.L.G. (2007) Ethanol Steam Reforming over Ni/M_xO_y-Al₂O₃ (M = Ce, La, Zr and Mg) Catalysts: Influence of Support on the Hydrogen Production. *International Journal of Hydrogen Energy*, **32**, 1462-1471. <http://dx.doi.org/10.1016/j.ijhydene.2006.10.025>
 - [30] Hsiao, W.I., Lin, Y.S., Chen, Y.C. and Lee, C.S. (2007) The Effect of the Morphology of Nanocrystalline CeO₂ on Ethanol Reforming. *Chemical Physics Letters*, **441**, 294-299. <http://dx.doi.org/10.1016/j.cplett.2007.05.024>
 - [31] Ni, M., Leung, D.Y.C. and Leung, M.K.H. (2007) A Review on Reforming Bio-Ethanol for Hydrogen Production. *International Journal of Hydrogen Energy*, **32**, 3238-3247. <http://dx.doi.org/10.1016/j.ijhydene.2007.04.038>
 - [32] Frusteri, F. and Freni, S. (2007) Bio-Ethanol, a Suitable Fuel to Produce Hydrogen for a Molten Carbonate Fuel Cell. *Journal of Power Sources*, **173**, 200-209. <http://dx.doi.org/10.1016/j.jpowsour.2007.04.065>
 - [33] Campos-Skrobat, F.C., Rizzo-Domingues, R.C.P., Fernandes-Machado, N.R.C. and Cantao, M.P. (2008) Novel Zeolite-Supported Rhodium Catalysts for Ethanol Steam Reforming. *Journal of Power Sources*, **183**, 713-716. <http://dx.doi.org/10.1016/j.jpowsour.2008.05.066>
 - [34] Biswas, P. and Kunzru, D. (2008) Oxidative Steam Reforming of Ethanol over Ni/CeO₂-ZrO₂ Catalyst. *Chemical*

- Engineering Journal*, **136**, 41-49. <http://dx.doi.org/10.1016/j.cej.2007.03.057>
- [35] Denis, A., Grzegorzczak, W., Gac, W. and Machocki, A. (2008) Steam Reforming of Ethanol over Ni/Support Catalysts for Generation of Hydrogen for Fuel Cell Applications. *Catalysis Today*, **137**, 453-459. <http://dx.doi.org/10.1016/j.cattod.2008.03.006>
- [36] Zhang, B., Cai, W., Li, Y., Xu, Y. and Shen, W. (2008) Hydrogen Production by Steam Reforming of Ethanol over an Ir/CeO₂ Catalyst: Reaction Mechanism and Stability of the Catalyst. *International Journal of Hydrogen Energy*, **33**, 4377-4386. <http://dx.doi.org/10.1016/j.ijhydene.2008.05.022>
- [37] Vizcaino, A.J., Arena, P., Baronetti, G., Carrero, A., Calles, J.A., Laborde, M.A. and Amadeo, N. (2008) Ethanol Steam Reforming on Ni/Al₂O₃ Catalysts: Effect of Mg Addition. *International Journal of Hydrogen Energy*, **33**, 3489-3492. <http://dx.doi.org/10.1016/j.ijhydene.2007.12.012>
- [38] Ren-Xuan, Y., Chuang, K.-H. and Ming-Yen, W. (2014) Hydrogen Production through Methanol Steam Reforming: Effect of Synthesis Parameters on Ni-Cu/CaO-SiO₂ Catalysts Activity. *International Journal of Hydrogen Energy*, **39**, 19494-19501. <http://dx.doi.org/10.1016/j.ijhydene.2014.09.140>
- [39] Bizkarra, K., Barrio, V.L., Yartu, A., Requies, J., Arias, P.L. and Cambra, J.F. (2015) Hydrogen Production from *n*-Butanol over Alumina and Modified Alumina Nickel Catalysts. *International Journal of Hydrogen Energy*, **40**, 5272-5280. <http://dx.doi.org/10.1016/j.ijhydene.2015.01.055>
- [40] Silva, P.P., Ferreira, R.A., Nunes, J.F., Sousa, J.A., Romanielo, L.L., Noronha, F.B. and Hori, C.E. (2015) Production of Hydrogen from the Steam and Oxidative Reforming LPG: Thermodynamic and Experimental Study. *Brazilian Journal of Chemical Engineering*, **32**, 647-662. <http://dx.doi.org/10.1590/0104-6632.20150323s00003441>
- [41] Osorio-Vargasa, P., Camposb, C.H., Navarroc, R.M., Fierroc, J.L.G. and Patricio Reyesa, P. (2015) Rh/Al₂O₃-La₂O₃ Catalysts Promoted with CeO₂ for Ethanol Steamreforming Reaction. *Journal of Molecular Catalysis A: Chemical*, **407**, 169-181. <http://dx.doi.org/10.1016/j.molcata.2015.06.031>
- [42] Ayodele, B.V., Khan, M.R. and Cheng, C.K. (2015) Syngas Production from CO₂ Reforming of Methane over Ceria Supported Cobalt Catalyst: Effects of Reactants Partial Pressure. *Journal of Natural Gas Science and Engineering*, **27**, 1016-1023. <http://dx.doi.org/10.1016/j.jngse.2015.09.049>
- [43] Marinhoa, A.L., Rabelo-Netob, R.C., Noronhab, F.B. and Mattosa, L.V. (2016) Steam Reforming of Ethanol over Ni-Based Catalysts Obtained from LaNiO₃ and LaNiO₃/CeSiO₂ Perovskite-Type Oxides for the Production of Hydrogen. *Applied Catalysis A: General*, **520**, 53-64. <http://dx.doi.org/10.1016/j.apcata.2016.03.032>
- [44] Levent, M., Küçük, Ö. and Çalban, T. (2008) Hydrogen Production with Catalytic Coal-Steam Gasification Process. *7th National Clean Energy Symposium(UTES 2008)*, İstanbul, 17-19 December 2008, 555-563.
- [45] Levent, M., Ağbaba, M. and Şahin, Y. (2009) Hydrogen Production with Ethanol-Steam Reforming Process in a Fixed Bed Reactor over Commercial BASF Catalyst. *5th International Advanced Technologies Symposium (IATS'09)*, Karabük University, 13-15 May 2009, 1756-1761.
- [46] Ağbaba, M., Levent, M. and Şahin, Y. (2009) Hydrogen Production by Propane-Steam Reforming Process in a Fixed Bed Reactor. *Nuclear and Renewable Energy Sources with International Participation Symposium*, Gazi University, 28-29 September 2009, 1-6.
- [47] Ağbaba, M., Levent, M. and Şahin, Y. (2014) Production of Synthesis Gases from Catalytic Steam Reforming of Ethanol and Propane Processes. *2014 13th International Conference on Clean Energy (ICCE 2014)*, İstanbul, 8-12 June 2014, 1312-1321.
- [48] Ağbaba, M. (2013) Catalytic Hydrogen Production with Ethanol and Propane Steam Reforming Process. PhD Thesis, Graduate School of Natural and Applied Science, Atatürk University, Erzurum.
- [49] Fogler, H.S. (1999) Elements of Chemical Reaction Engineering. 3rd Edition, Prentice-Hall Inc., Upper Saddle River.
- [50] Guzzi, L. and Erdöhelyi, A. (2007) Catalysis for Alternative Energy Generation. Chapter 4, Reforming of Ethanol, Springer, New York, 129-174.
- [51] Spivey, J.J. and Dooley, K.M. (2007) Catalysis: Specialist Periodical Reports. Vol. 20, The Royal Society of Chemistry Publishing, MPG Books Ltd., Cambridge, 65-106.
- [52] Mathure, P.J., Ganguly, S., Patwardhan, A.V. and Saha, R.K. (2007) Steam Reforming of Ethanol Using a Commercial Nickel-Based Catalyst. *Industrial & Engineering Chemistry Research*, **46**, 8471-8479. <http://dx.doi.org/10.1021/ie070321k>

X_{EtOH} : mole fraction of ethanol (dimensionless)
 n_{EtOH} : mole number of ethanol (moles)
 Y_{H_2} : mole fraction of hydrogen (dimensionless)
 n_{H_2} : mole number of hydrogen (moles)
 R_{EtOH} : reaction rate based on ethanol consuming (mole ethanol/gr.cat.min)
 k : reaction rate constant (1/min)
 C_{EtOH} : concentration of ethanol at any time (mol/l)
 P_{EtOH} : partial pressure of ethanol (bar)
 R : gas constant(8.314 J/mol. $^{\circ}\text{K}$)
 T : absolute temperature ($^{\circ}\text{K}$)
 A : frequency(Arrhenius) constant (dimensionless)
 E_A : activation energy (kJ/mol)
 W : mass of loaded Catalyst (gr)
 F_{EtOH} : molar flowrate of ethanol (mol/min)

**Scientific Research Publishing**

Submit or recommend next manuscript to SCIRP and we will provide best service for you:

Accepting pre-submission inquiries through Email, Facebook, LinkedIn, Twitter, etc.

A wide selection of journals (inclusive of 9 subjects, more than 200 journals)

Providing 24-hour high-quality service

User-friendly online submission system

Fair and swift peer-review system

Efficient typesetting and proofreading procedure

Display of the result of downloads and visits, as well as the number of cited articles

Maximum dissemination of your research work

Submit your manuscript at: <http://papersubmission.scirp.org/>