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Catalytic Dry Reforming of Natural Gas for Synthesis Gas Production over Ru/γ-Al$_2$O$_3$ Catalyst.

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Abstract

Catalytic reforming of natural gas with carbon dioxide to produce syngas has been investigated over ruthenium (0.5 wt %) supported on γ-alumina. Capillary gas chromatography was used to detect and evaluate the hydrocarbons and non-hydrocarbons in the natural gas before and after reaction. This research aims to study the effect of the space velocity and temperature on the conversion of carbon dioxide and all the components of the natural gas. The space velocity 36000 ml g^{-1}h^{-1} and the temperature 800^{o}C are the optimum operating conditions giving the highest conversion of both the methane and carbon dioxide, but the space velocity 18000 ml g^{-1} h^{-1} and the temperature at 800^{o}C are the preferred conditions for production of the hydrogen and carbon monoxide (synthesis gas).

Keywords: Catalytic reforming, natural gas, synthesis gas, Ruthenium, γ- alumina, capillary gas chromatography

INTRODUCTION

Synthesis gas with equal H_2/CO molar ratio can be used to produce valuable oxygenated chemicals and long-chain hydrocarbons following Fischer–Tropsch synthesis (Ross et al., 1996; Wender 1996). Direct synthesis of dimethylether, which is considered as one of the best alternates of diesel fuel, also requires a synthesis gas containing a similar ratio of hydrogen to CO. Reforming of methane with carbon dioxide (dry reforming) is an attractive reaction for the production of synthesis gas with this required composition than steam reforming or partial oxidation reaction of methane (Nimwattanakul et al., 2003; Jeong et al., 2006). Based on its high endothermicity, this reforming process can also be applied in chemical energy transmission systems (CETS) to convert fossil, nuclear and solar energy into chemical energy (Richardson and Paripatyadar, 1990). Natural gas (N.G) reforming is questionable as to whether CH_4/CO_2 reforming can contribute to a solution of greenhouse problems. Reducing of sources of CH_4 and CO_2 greenhouse gases could lead to a decline in the rate of the global warming, reducing the danger of dramatic climate change (Rostrup-Nielsen et al., 1997). Group VIII metals are reported to be effective catalysts in this reaction. The conventional Ni based CO_2 reforming catalysts tend to be coked due to the formation of stable nickel carbide on the surface of Ni catalysts to give whisker carbon (Rostrup-Nielsen and Hansen, 1993).

In the case of CO_2/CH_4 reforming there is a greater potential for carbon formation, primarily due to the lower H/C ratio of this system. Thermodynamic analysis of the CO_2/CH_4 reforming reaction system shows that carbon formation is possible over a wide range of reaction conditions of commercial interest (Edwards and Maitra, 1995). The combination of a metal and a support greatly affected catalytic activity and carbon deposition of this reaction without any or with only slight carbon deposition (Matsui et al., 1999). Solymosi et al. (1991) reported that the order is Ru>Pd>Rh>Pt>Ir when Al_2O_3 was used as a support. On the other hand; the order of catalytic activity for the dry methane reforming at 723K on a turnover frequency basis was found to be:- Rh> Ni>Ir>Ru~ Pt>Co] (Ferreira-Aparicio et al., 1998). Richardson and Paripatyadar (1990) studied the ruthenium and rhodium metals (0.5wt%) supported on γ-Al_2O_3 for reforming of methane with carbon dioxide at low ratios of CO_2/CH_4 in the temperature range 600 – 800ºC and GHSV 51.1 x $10^{-3}h^{-1}$ .They confirmed that Rh and Ru have comparable activities but that Rh was much more stable. However; dry reforming requires the use of stable and effective catalysts, resistant to coking; hence investigations should be focused on the metal activity, the resistance to coke formation and the type of the support that improves the catalyst efficiency (Garcìa-Diéguez et al., 2010).

The present work focused on the effects of the Ru/γ-Al_2O_3 catalyst on the reforming activity of carbon dioxide and natural gas components, in addition, the effect of different gas velocities and temperatures on the reforming process in order to obtain the optimum conditions for maximum conversion of hydrogen and carbon monoxide.

EXPERIMENTAL

Catalyst Preparation

The Ru Catalyst was prepared using incipient wetness impregnation techniques (Ferreira- Aparicio et al., 1998). γ-alumina (Puralox, Condea) was used as a support. Impregnation was carried out with aqueous solution of $RuCl_3.3H_2O$ (Merck) with 0.5% wt metal loading .Then, the catalyst was dried overnight at 110ºC and calcined with air in a muffle furnace at 500ºC for 3h. Before reaction and characterization tests, the catalyst was submitted to a standard reduction pretreatment by heating in pure hydrogen at a rate of 20 ml/min at 500ºC for 7 h.

Reaction apparatus

A quartz tube flow reactor (800 mm overall length, 13 mm in diameter) filled with 2 gm of catalyst between two layers of ceramic fibers was placed in a ventilated oven. A K-type thermocouple located inside the catalytic bed to control the reaction temperature was used. The reaction mixture of N.G.:CO_2:N_2 in proportions 1:1:4 regulated by mass flow controllers was adjusted to give flow rates corresponding to gas hourly space velocities: 18000, 36000, 45000, 60000 ml g^{-1} h^{-1} respectively. The mixture of reactants was introduced by switching a four-way valve located at the reactor inlet. Reaction temperatures from 600 to 800ºC were examined at atmospheric pressure. An ice-cold trap was set between the reactor exit and gas sampling to remove the water and condensable formed during reaction. After shifting from one temperature to another and the latter was reached, the catalyst bed was left for at least 15 min to be sure that the temperature was almost constant through the catalyst bed. After another 30 min products were received in gas samplers. The experimental setup is as shown in Fig. 1.

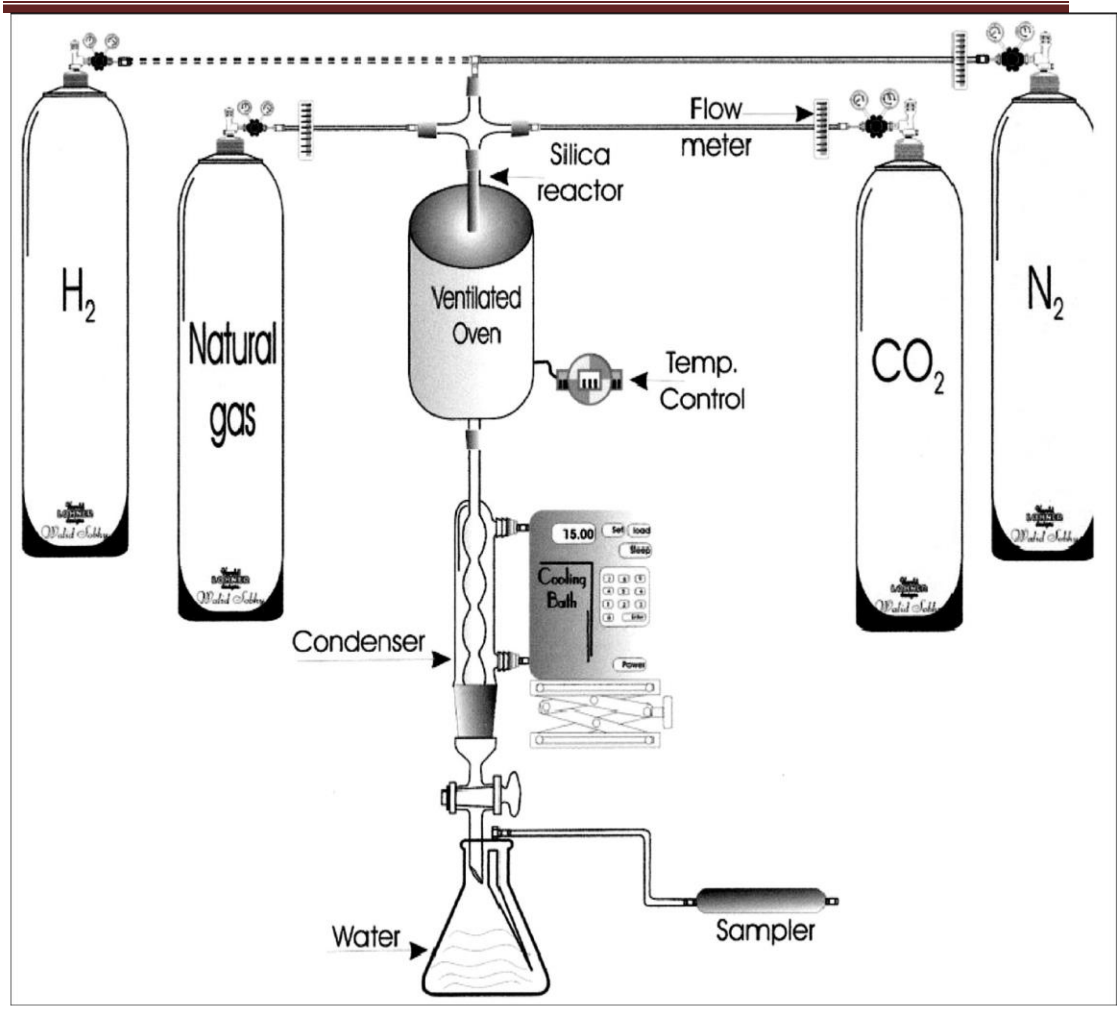

Fig. 1. Experimental Setup.

Gas chromatographic analysis

The used natural gas components (N_2, CO_2 and C_1 – C_7) and the produced gases (H_2 and CO) were analyzed using an Agilent 6890 plus, HP, gas chromatograph, equipped with thermal conductivity (TCD) and flame ionization (FID) detectors, and a fused silica plot Q capillary column (15 meter in length and 0.35 mm internal diameter). A packed column DC 200 of stainless steel in type (10 feet in length and 1/8 inch in diameter) was attached to the TCD and the capillary column plot Q (30 meter in length and 0.35 mm in diameter) was attached to the FID, The injector and detector temperatures were 200 and 250ºC respectively. The elution of the studied gas mixtures was achieved with temperature programming from 60 to 200ºC at a rate 10ºC min^{-1}. Nitrogen (oxygen-free) was used as a carrier gas for the analysis of the natural gas, while helium for the detection of CO and H_2. Flow rates were measured from the end of the column with a soap bubble flow meter. Methane as an unattained marker was used to correct the dead volume in the column in the case of FID, and air in the case of TCD. The quantitative analysis of the liberated gas mixture was achieved using standard natural gas sample of known composition and according to the standard method ASTM D-1945 (2003).

The areas under the resolved chromatographic profiles were estimated by integration using a connected Epson data station unit.

RESULTS AND DISCUSSIONS

The distribution of the hydrocarbons and the non hydrocarbons components of the studied natural gas was determined by capillary gas chromatography were given in Table 1. It has been found that the natural gas contains mainly methane (93 mol %), the remaining paraffins represent about 6 mol %. The inorganic gases (nitrogen and carbon dioxide) represent 0.82 mol %. The natural gas contains a small amount of CO_2 (0.45 mol %) it has a little effect as an oxidizing agent compared with the carbon dioxide used as feed with natural gas.

Table 1. Composition of the used natural gas.

Component	Mol.%	Wt %
N_2	0.368	0.582
C_1	93.041	84.254
CO_2	0.448	1.113
C_2	3.513	5.965
C_3	1.469	3.656
i-C_4	0.324	1.064
n-C_4	0.366	1.202
i-C_5	0.137	0.559
n-C_5	0.105	0.428
C_6	0.146	0.711
C_7	0.083	0.468
Total	100.000	100.000

The studied catalyst Ru/γ-Al_2O_3 was tested under atmospheric pressure, the feed gases (N.G.: CO_2: N_2 = 1:1:4) were introduced into the catalyst bed at the prescribed space velocities and temperatures in order to determine the optimum conditions required for the N.G. reforming with CO_2 reaction, which give the best H_2-selectivity, CO-selectivity, as well as, CH_4 and CO_2 conversions. Also, the behavior of heavy hydrocarbons present in the natural gas towards CO_2 reforming reaction was studied.

CH_4 and CO_2 Conversions

The 0.5 % Ru/γ-Al_2O_3 catalyst exhibit reactivity with varying degrees at the whole temperature range. At constant flow rate, the activity of catalyst increased as temperature increased, this occurs because CO_2 reforming reaction is a highly endothermic reaction (Yokota et al., 2000):-

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H^o_{298} = 247 \text{ kJ/mol}$$

At a constant space velocity CH_4 & CO_2 conversions increased as the temperatures increased from 600ºC to 800ºC. On the other hand; at a constant temperature, CH_4 & CO_2 conversions increased in the order of 36000 > 45000 > 60000 > 18000 ccg^{-1}h^{-1}. However; for CO_2 at 600ºC the maximum conversion was shifted to a higher space velocity (45000 ccg^{-1}h^{-1}) as shown in Fig. 2 and the data given in Table 2.

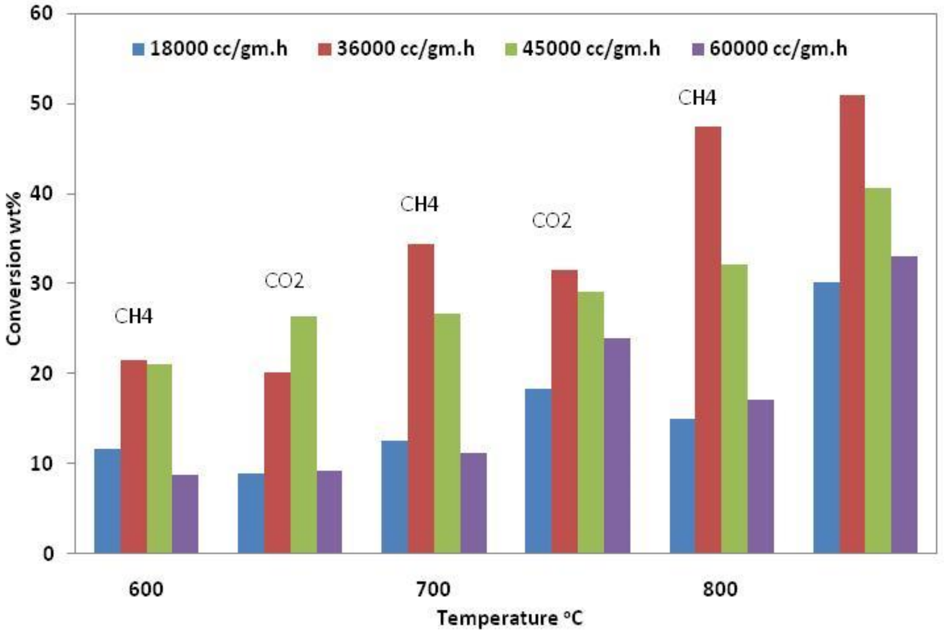

Fig. 2. Conversion of CH_4 and CO_2 on Ru/γ-Al_2O_3 catalyst at different temperatures and space velocities.

Conversion with respect to CH_4 & CO_2 was achieved maximally at temperature of 800ºC and space velocity 36000cc g^{-1} h^{-1}. This may be related to formation of CH_x fragments, its reactivity and its amount, ability of catalyst to insert them in the reaction all these factors contribute to determine the optimized conditions for the reaction (Osaki et al., 1995; 1996; Richardson and Paripatyadar; 1990)

Matsui et al. (1999), Osaki et al (1995; 1996), concluded that CH_4 was dissociatively adsorbed on the catalysts to release gaseous H_2 and that the resultant adsorbed hydrocarbon species (CH_x) gradually reacted with CO_2 to produce CO and H_2. These results suggest that CO_2 reforming of methane proceeded by rapid hydrogen abstraction from CH_4 to give H_2 and CH_x– Ru species, followed by a slow reaction of CO_2 with Ru–CH_x. The increase of conversion with decreasing space velocity from 60000 cc g^{-1}h^{-1} to 36000 cc g^{-1}h^{-1} is normally expected as the contact time increased. But the final decrease in conversion with further decrease in space velocity (increase in contact time) can be explained by catalyst deactivation due to sintering. For Ru-catalysts a sintering of the metallic phase has been detected by Ferreir-Aparicio et al. (1998). As given in Table 2 the conversion of CO_2 was always higher than the conversion of CH_4 at the same conditions although a feed ratio of unity was used. This is in agreement with Zhang et al. (1996). Referring to Table 1, for Ru/γ-Al_2O_3 catalyst at a space velocity of 18000 cc g^{-1}h^{-1}& 800ºC, CH_4 conversion was 15 %, while, CO_2

conversion was 30.09 % this occurs because CO_2 is also consumed in RWGS (reverse water gas shift reaction) and Boudouard reaction so its conversion is usually higher than CH_4 conversion (Portugal et al., 2000).

Table 2. Conversion of CO_2 and CH_4 on Ru/γ-Al_2O_3 at the studied conditions

Temperature°C	**600°C**		**700°C**		**800°C**	
Space velocity cc/gm.h	**CH_4**	**CO_2**	**CH_4**	**CO_2**	**CH_4**	**CO_2**
18000	11.74	8.96	12.56	18.38	15	30.09
36000	21.5	20.13	34.46	31.54	47.42	50.95
45000	21.05	26.31	26.62	29.05	32.17	40.65
60000	8.83	9.17	11.28	23.99	17.1	33.08

Conversion of heavy components

Ethane and propane conversion

The conversion of ethane and propane increased with increasing the temperature, 800°C is the most efficient degree giving high conversion percentage as shown in Figs. 3a and 4a because the CO_2-reforming of N.G. is a highly endothermic reaction.

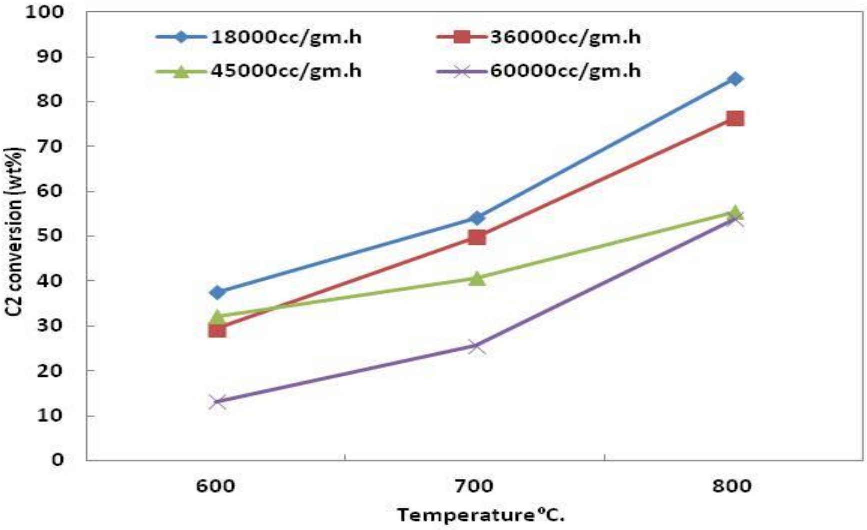

Fig. 3a. Conversion versus temperatures of C2-alkane on Ru/γ-Al2O3 catalyst at different space velocities.

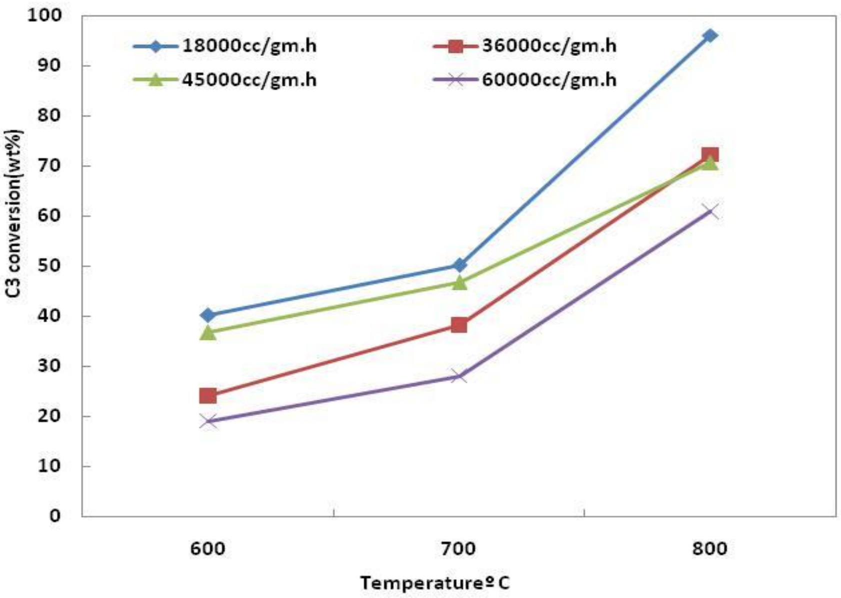

Fig. 4a. Conversion versus temperatures of C3-alkane on Ru/γ-Al2O3 catalyst at different space velocities.

At a constant temperature; the conversion C_2 decreased in the sequence of increasing of space velocity i.e. conversion at 18000 > 36000 > 45000 > 60000 ccg-1h-1 where the contact time was (0 .027, 0.013, 0.011, 0.008 min^{-1}) respectively. But for the conversion of C_3 the sequence was slightly different 18000 > 45000 > 36000 > 60000 $ccg^{-1}h^{-1}$ at the temperature 600ºC & 700ºC, as shown in Figs. 3b and 4b; Table 3.

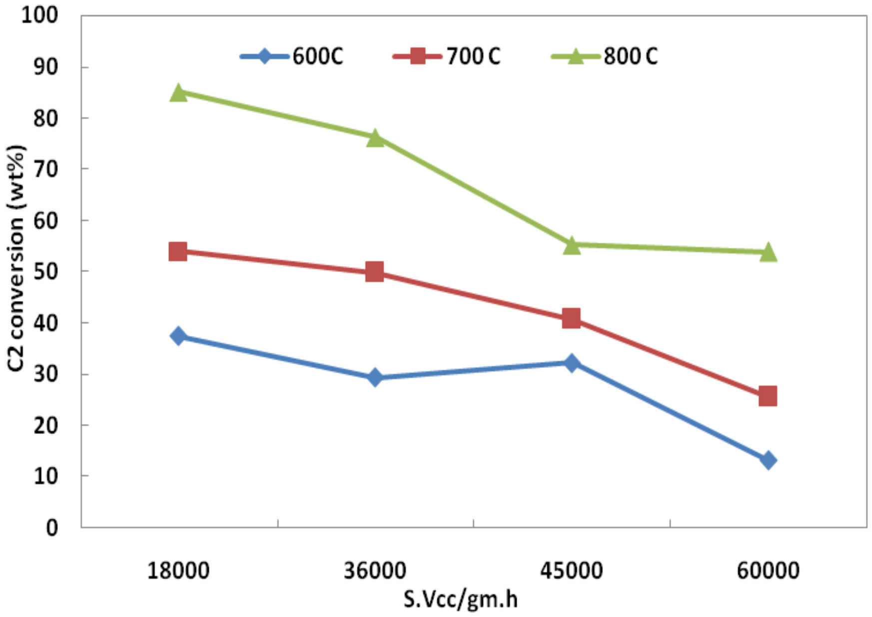

Fig. 3b. Conversion versus space velocities of C2-alkane on Ru/γ-Al2O3 catalyst at different temperatures.

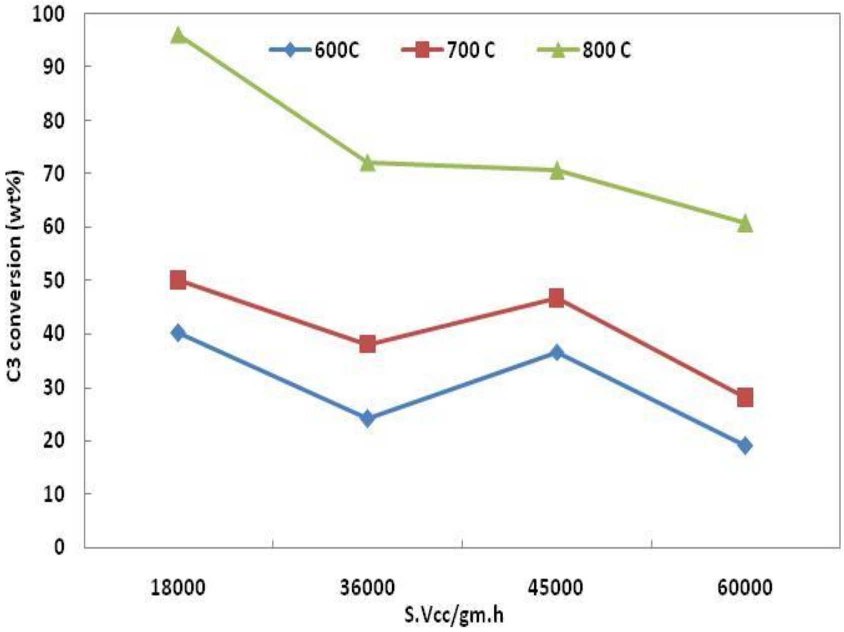

Fig. 4b. Conversion versus space velocities of C3-alkane on Ru/γ-Al2O3 catalyst at different temperatures.

Generally; the space velocity 18000 ccg^{-1}h^{-1} and the temperature 800ºC are the optimum conditions for obtaining the highest conversion percentage of ethane and propane.

Conversion of butanes and pentanes (normal and iso-) compounds

The butanes (normal and iso-) and pentanes (normal and iso-) represent 0.690 mol% and 0.342 mol% respectively in the composition of studied natural gas, their conversion differs with the working temperature and space velocity. The conversions of both components increased with decreasing the space velocity at all the studied temperatures; the space velocity 18000 ccg^{-1}h^{-1} exhibited the most efficient velocity for complete conversion of both butanes and heptanes because this velocity offered a suitable enough time for complete reaction.

It is clear that the temperature 800ºC for butanes (normal and iso-) and pentanes (normal and iso-) is the optimum temperature for conversion at all the studied space velocities, as shown in Figs. 5A-C and 6A-C.

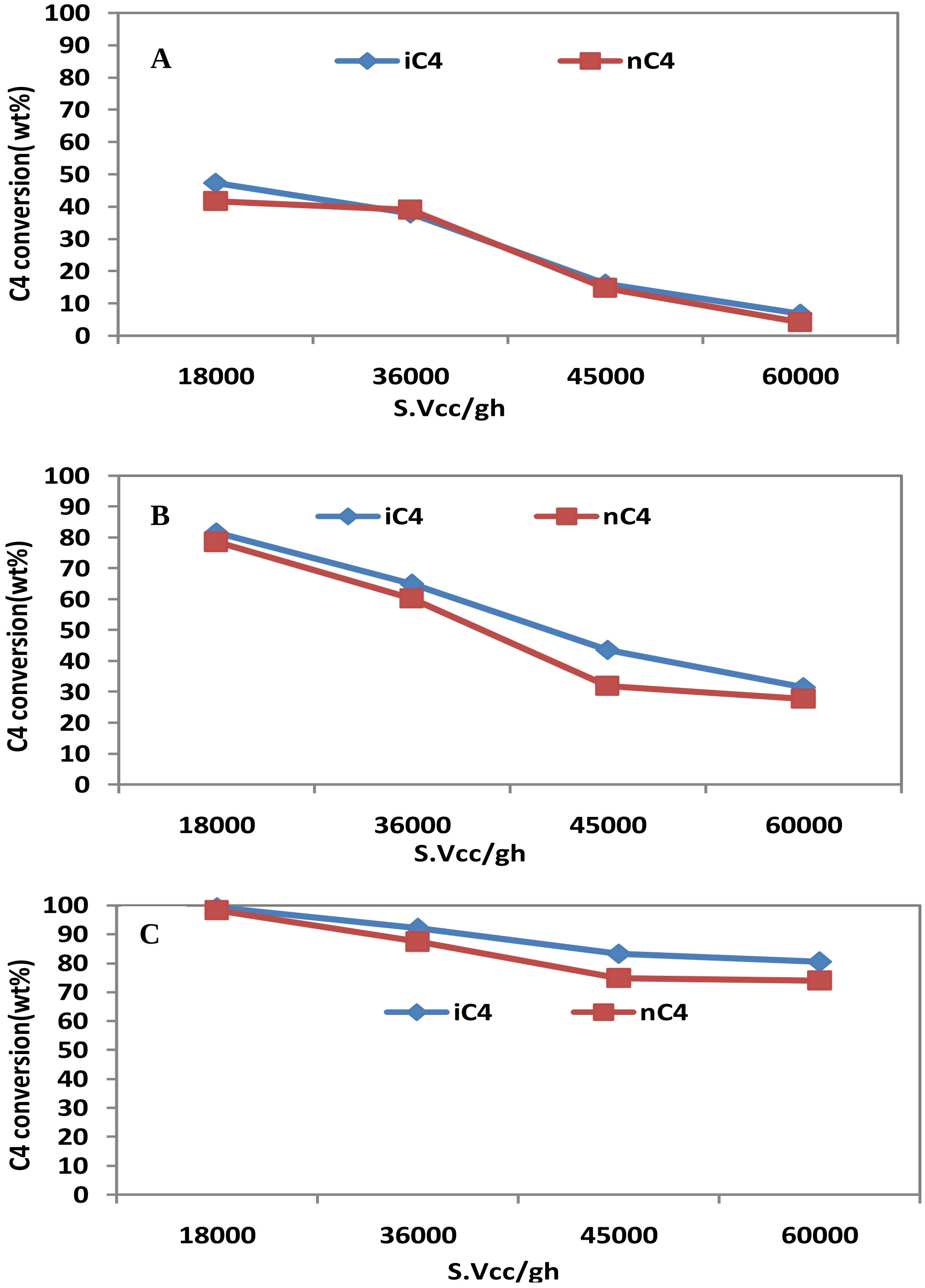

Fig. 5A-C. Conversion versus space velocities of C4 – alkanes on Ru/γ-Al2O3 catalyst at A (600) , B (700) , C (800)ºC.

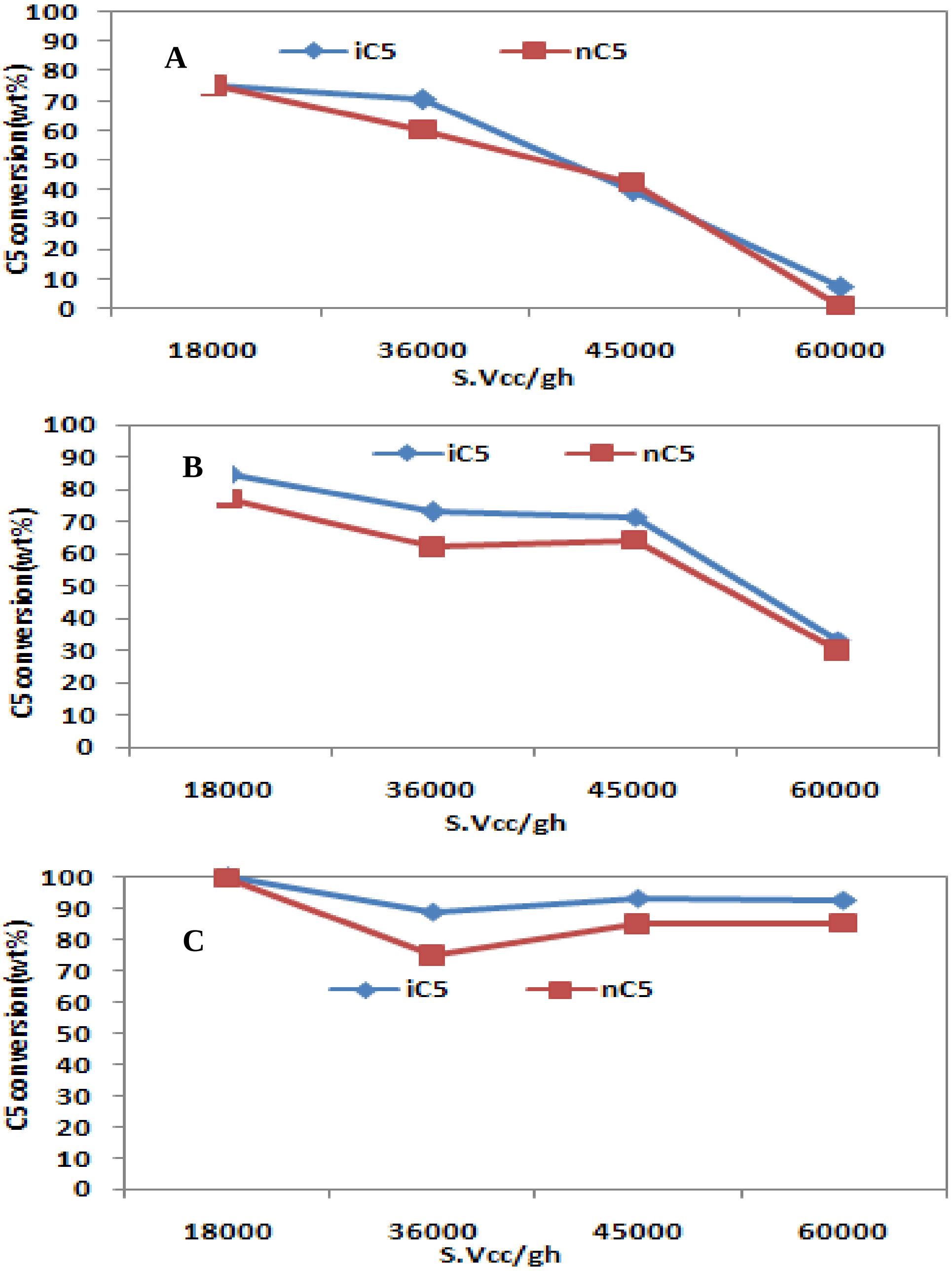

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Fig. 6 A-C. Conversion versus space velocities of C5 – alkanes on Ru /Al2O3 catalyst at temperatures A (600), B (700), C (800)ºC.

At a constant temperature, it is clear that the butanes (normal and iso-) and pentanes (normal and iso-) conversion decreased in the sequence of increasing the space velocity .i.e. conversion at 18000 > 36000 > 45000 > 60000 ccg^{-1}h^{-1} in the order of decreasing the contact time, as shown in Fig.6A-C and 87A-C. However; the decrease in conversion with increasing space velocity was not very pronounced for pentanes at 800ºC Fig.8C and the data given in Tables 3.
Also, at the four different space velocities the conversion of iso-butanes and iso-pentanes was generally higher than n- butanes and n-pentanes conversion at all

temperatures Table 3, this may be occur because the iso-components are more active due to the branching in the chain .

Generally, the space velocity 18000 ccg^{-1}h^{-1} and the temperature 800ºC are the optimum condition for obtaining the highest conversion percentage of the butanes (normal and iso-) and pentanes (normal and iso-).

Hexanes and heptanes conversion

The conversion of hexanes and heptanes increased with increasing the temperature, 800ºC is the most efficient degree giving high conversion percentage as shown in Figs. 7 and 8 because the CO_2-reforming of N.G. is a highly endothermic reaction.

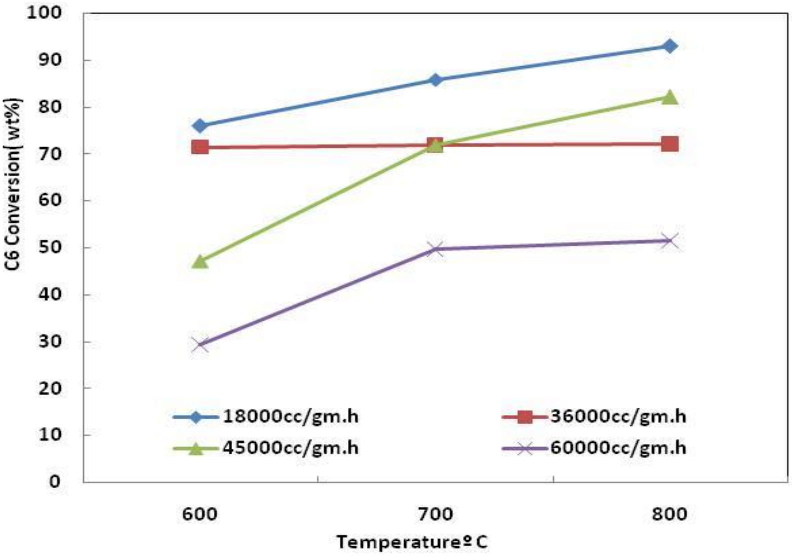

Fig. 7. Conversion versus temperatures of C6 – alkanes on Ru/γ-Al2O3 catalyst at different space velocities.

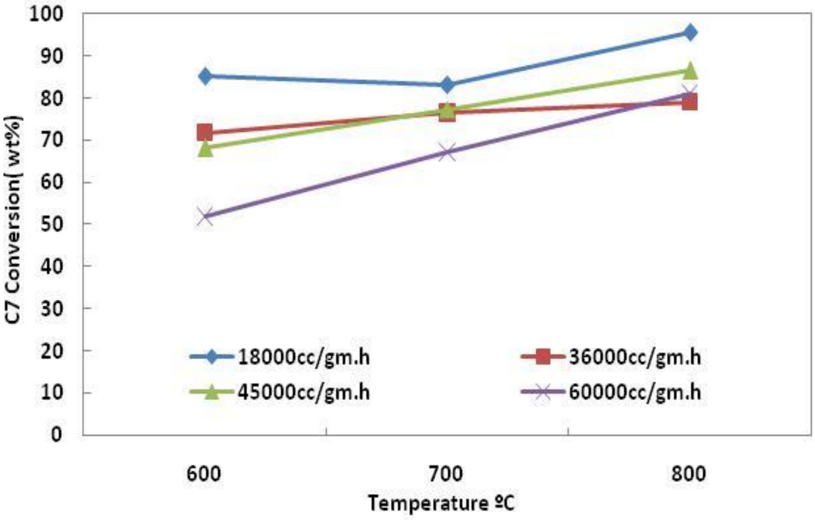

Fig. 8. Conversion versus temperatures of C7 –alkanes on Ru/γ-Al2O3 catalyst at different space velocities.

The conversion of hexanes and heptanes increased with decreasing the space velocities which is the order of increasing the contact time.

At constant temperature, the conversion decreased in the sequence of increasing of space velocity .i.e. conversion at 18000 > 36000 > 45000 > 60000 cc.gm^{-1}h^{-1} in the order of contact time decrease (0 .027, 0.013, 0.011, 0.008 min^{-1}) respectively, Table 3. Generally, the space velocity 18000 ccg^{-1}h^{-1} and the temperature 800ºC are the optimum condition for obtaining the highest conversion percentage of the hexanes and heptanes.

Table 3. Conversion of C_2^+ to C_7^+ natural gas alkanes on Ru/γ-Al_2O_3catalyst at the studied Conditions.

Temperatures	**600^{o}C**		**700^{o}C**		**800^{o}C**	
Space Velocities ccg^{-1}.h^{-1}	C_2	C_3	C_2	C_3	C_2	C_3
18000	**37.45**	40.16	**53.97**	50.08	**85.16**	96.18
36000	**29.32**	24.09	**49.81**	38.16	**76.3**	72.23
45000	**32.21**	36.72	**40.76**	46.68	**55.31**	70.64
60000	**13.14**	19.01	**25.55**	28.03	**53.84**	60.81
Temperatures	**600^{o}C**		**700^{o}C**		**800^{o}C**	
Space Velocities ccg^{-1}.h^{-1}	*i*-C_4	*n*-C_4	*i*-C_4	*n*-C_4	*i*-C_4	*n*-C_4
18000	**47.41**	41.68	**81.6**	78.6	**99.32**	98.18
36000	**37.84**	39.09	**64.94**	60.34	**92.03**	87.38
45000	**16.2**	14.84	**43.67**	31.95	**83.19**	74.87
60000	**6.94**	4.21	**31.6**	27.84	**80.4**	73.97
Temperatures	**600^{o}C**		**700^{o}C**		**800^{o}C**	
Space Velocities ccg^{-1}.h^{-1}	*i*-C_5	*n*-C_5	*i*-C_5	*n*-C_5	*i*-C_5	*n*-C_5
18000	**75.45**	75.08	**84.35**	77.03	**100**	99.67
36000	**70.45**	60.28	**72.98**	62.01	**89.01**	75.1
45000	**39.52**	42.27	**71.34**	64.11	**93.6**	85.11
60000	**7.17**	0.88	**33.13**	29.78	**92.68**	85.42
Temperatures	**600 ^{o}C**		**700^{o}C**		**800^{o}C**	
Space Velocities ccg^{-1}.h^{-1}	C_6^+	C_7^+	C_6^+	C_7^+	C_6^+	C_7^+
18000	**75.97**	85.11	**85.9**	83.03	**92.98**	95.56
36000	**71.46**	71.8	**71.76**	76.43	**72.06**	79.15
45000	**47.17**	68.19	**71.95**	77.33	**82.1**	86.47
60000	**29.25**	51.8	**49.71**	67.16	**51.47**	80.94

Formation of syngas (H2 and CO)

The H_2 and CO selectivity using Ru/γ-Al_2O_3 catalyst at different conditions are given in Table 4. No hydrogen was present at the tested temperatures of 600ºC and 700ºC for all space velocities, but CO was always detected at the different conditions as given in Table 4. Only for space velocities of 18000, 36000 $ccg^{-1}h^{-1}$ and at 800ºC reaction temperature, Ru/γ-Al_2O_3 catalyst showed fair selectivity to H_2.The selectivity of CO increased as a function of temperature for all the studied velocities. Also; at constant temperature the selectivity of both H_2 and CO decreased with increasing the space velocity.

Generally; H_2/CO ratio < 1 is observed due to the higher CO selectivity as compared to that of H_2, in agreement with (Wang and Ruckenstein, 2000); as given in Table 4 this aspect can be explained by considering that CO is also formed as a product in other chemical reactions (Portugal et al., 2000). Hydrogen produced as a result of the reforming reaction could be consumed by the RWGS which is more active at lower temperature (Portugal et al., 2000; Mark and Maier, 1996). This is shown through the following set of reactions.

Hydrogen can be produced by the dry reforming reaction (DR):-

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2 \text{ (DR)}$$

Or by methane cracking:-

$$CH_4 \rightarrow C + 2H_2$$

But CO can be supplied by the dry reforming reaction (DR):-

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2 \text{ (DR)}$$

OR Boudouard reaction:-

$$CO_2 + C = 2CO$$

OR (RWGS) reaction:-

$$CO_2 + H_2 = CO + H_2O$$

OR steam reforming reaction:-

$$CH_4 + H_2O = CO + 3H_2$$

Table 4. H_2 and CO selectivity of Ru/γ-Al_2O_3 catalyst at different temperatures and space velocities.

Temperatures ºC	**600ºC**			**700ºC**			**800ºC**		
Space Velocities $ccg^{-1}.h^{-1}$	**H_2%**	**CO%**	**H_2/CO**	**H_2%**	**CO%**	**H_2/CO**	**H_2%**	**CO%**	**H_2/CO**
18000	-	0.91	-	-	1.48	-	5.31	14.28	0.372
36000	-	0.72	-	-	1.07	-	2.54	7.82	0.32
45000	-	0.56	-	-	0.66	-	-	5.98	-
60000	-	0.22	-	-	0.42	-	-	5.22	-

Generally, the space velocity 18000$ccg^{-1}h^{-1}$ and the temperature 800ºC are the optimum conditions for obtaining the highest individual selectivity for both H_2

and CO. These same conditions are the best to produce the highest ratio (0.372) of H_2/CO as shown in Table 4.

CONCLUSIONS

1. The space velocity 36000 $ccg^{-1}h^{-1}$ and the temperature 800ºC are the optimum condition resulting in the maximum conversion of methane but, the space velocity 18000 $ccg^{-1}h^{-1}$ and the temperature 800ºC are the optimum condition resulting in the maximum conversion of the other heavy hydrocarbons in the natural gas (ethane, propane, butanes, pentanes, hexanes, and heptanes).
2. The Ru/γ-Al_2O_3 selectivity with respect to H_2 and CO was achieved maximally at temperature of 800ºC and space velocity 18000 $ccg^{-1}h^{-1}$.
3. Maximum (H_2/CO) ratio was achieved at the optimum conditions, space
4. velocity 18000 $ccg^{-1}h^{-1}$ and the temperature 800ºC.

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