

CHAPTER 4
RESULTS AND DISCUSSION

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The distribution of the hydrocarbons and the inorganic gases of the used natural gas were determined by a high sensitive gas chromatograph using a standard natural gas of known composition, the composition determined is given in table (4.1).

It has been found that the studied natural gas contains mainly methane, the remaining paraffins represent about 6.143 mol % and the inorganic gases (nitrogen and carbon dioxide) represent 0.816 mol %. The investigated natural gas contained very little amount of carbon dioxide about 0.448 mol % that has negligible effect compared with the used carbon dioxide as oxidizing agent.

Table (4.1): Composition of the used Natural gas

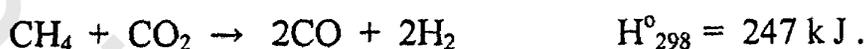
Component	Mol. %	Wt %
N ₂	0.368	0.582
C ₁	93.041	84.254
CO ₂	0.448	1.113
C ₂	3.513	5.965
C ₃	1.469	3.656
i-C ₄	0.324	1.064
n-C ₄	0.366	1.202
i-C ₅	0.137	0.559
n-C ₅	0.105	0.428
C ₆	0.146	0.711
C ₇	0.083	0.468
Total	100.000	100.000

4.1. Rh / γ -Al₂O₃ catalyst :-

4.1.1. CH₄ Conversion :-

The 0.5 % Rh / γ -Al₂O₃ catalyst exhibit reactivity with varying degrees at the whole temperature range .

At constant flow rate , the activity of catalyst was increased as temperature increased ,This occurs because CO₂ reforming reaction is a highly endothermic reaction (Yokota et al ; 2002) :-



At constant space velocity CH₄ conversion increased as the temperature increased from 600°C to 800°C as shown in Fig. (4.1 -a).

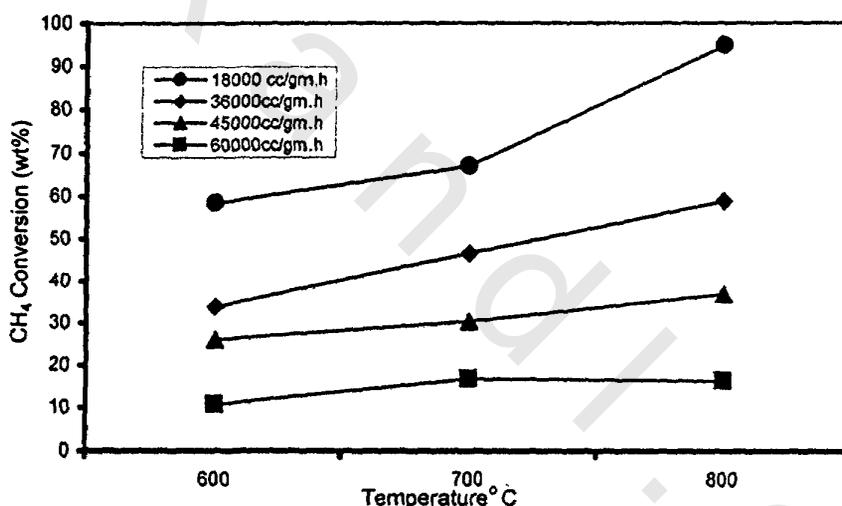


Fig. (4.1 -a) . Conversion versus temperatures of CH₄ on Rh / γ -Al₂O₃ catalyst at different space velocities .

At constant temperature , CH₄ – conversion increased as the space velocity decreased or contact time increased (i.e) CH₄ conversion increase in the order of 18000 > 36000 > 45000 > 60000 cc g⁻¹h⁻¹, where the contact time was (0 .027 , 0.013 , 0.011 , 0.008 min⁻¹) respectively , as shown in Fig. (4.1.b.) , and the data given in Table (4.2) .

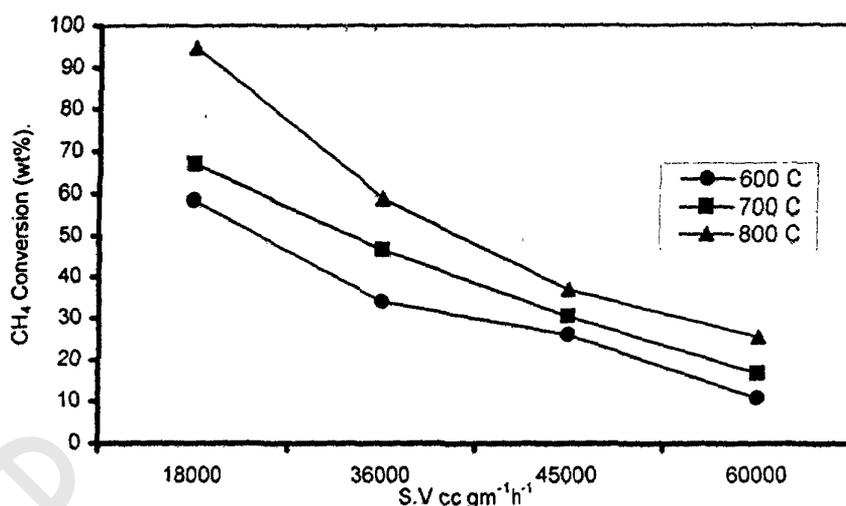


Fig.(4.1.b) . Conversion versus space velocities of CH₄ on Rh / γ -Al₂O₃ catalyst at different temperatures .

However ; the 0.5 % Rh / Al₂O₃ conversion with respect to CH₄ was achieved maximally at temperature of 800°C and space velocity 18000 cc g⁻¹h⁻¹ ; as shown in Fig.(4.1-a,b) and given in Table (4.2).

Rh-based catalysts are known to exhibit good stability for the whole temperature range, and are the most resistance to sintering and to carbon deposition , the high resistant of supported Rh - catalysts to deactivation by carbon deposition has been recently explained by a rapid reaction of CH_x fragments with the reactant CO₂(Ferreira-Aparicio et al ;1998) .

4. 1. 2. CO₂ Conversion :-

The 0.5% Rh / Al₂O₃ catalyst exhibit reactivity with varying degrees within the whole temperature range .

At constant flow rate , the activity of catalyst increased as temperature increased , This occur because CO₂ reforming reaction is a highly endothermic reaction (Yokota et al ; 2002) .

At a constant space velocity CO₂ conversion increased as the temperature increased from 600°C to 800°C as shown in Fig (4.2 -a) .

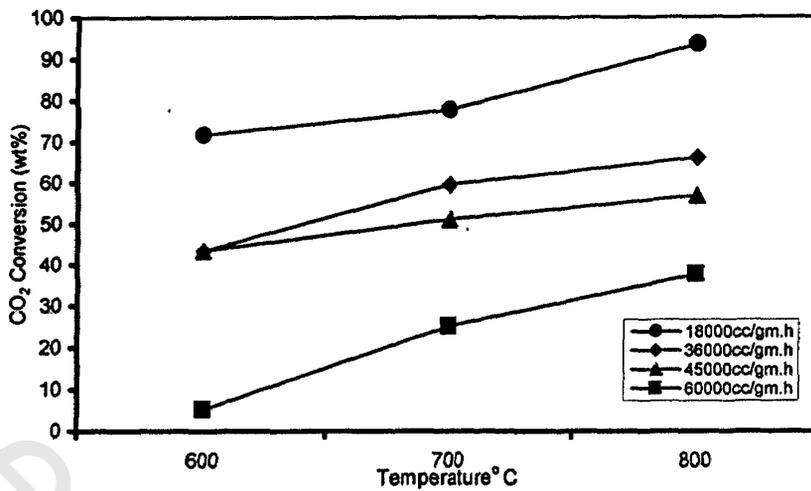


Fig.(4.2-a) . Converter versus temperatures of CO₂ on Rh / γ -Al₂O₃ catalyst at different space velocities .

At constant temperature , CO₂ – conversion increased as the space velocity decreased or contact time increased (i.e) CO₂ conversion increase in the order of 18000 > 36000 > 45000 > 60000 cc.g⁻¹.h⁻¹, where the contact time was (0.027 , 0.013 , 0.011 , 0.008 min⁻¹) respectively , as shown in Fig.(4.2-b) , Table (4.2) .

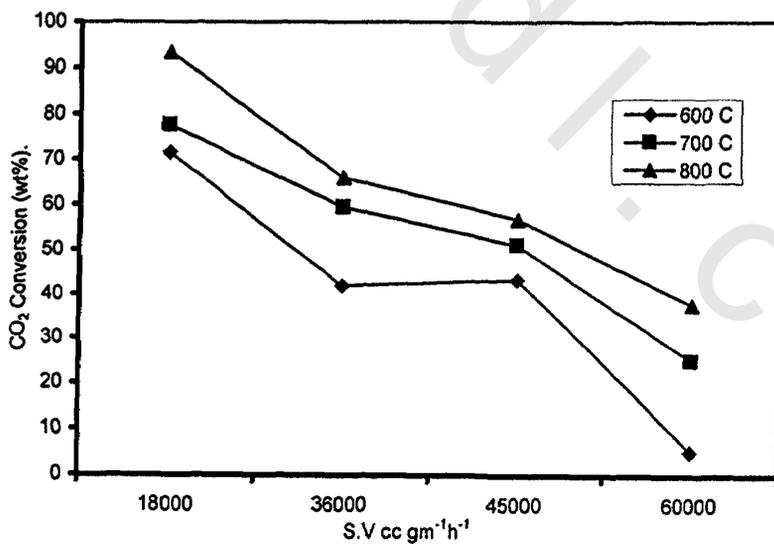
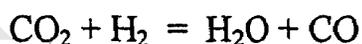


Fig.(4.2-b) . Conversion versus space velocities of CO₂ on Rh/ γ -Al₂O₃ catalyst at different temperatures .

However ; the catalyst 0.5 % Rh /Al₂O₃ achieved maximum conversion with respect to CO₂ at a temperature of 800°C and space velocity 18000 cc g⁻¹h⁻¹ ; as shown in Fig . (4.2-a , b) and the data given in Table (4.2) .

The conversion of CO₂ was always higher than the conversion of CH₄ , at the same conditions although a feed ratio of unity was used , the difference was more pronounced at low temperature in agreement with (Zhang et al ; 1996) , as given in table (4.2) , for example , for Rh /γ-Al₂O₃ catalyst at space velocity = 18000ccg⁻¹h⁻¹ , 600°C , CH₄ conversion was 58.47 % , while , CO₂ conversion was 71.62 % this occur due to RWGS (reverse water gas shift reaction) which take place at lower temperatures :-

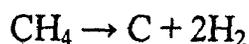


(i.e) there are different pathways for CO₂ to be consumed so its conversion is usually higher than CH₄ conversion (Portugal et al ; 2000) , (Bhat et al ; 1997) and (Mark et al ; 1996) .

The hydrogen can be supplied by the dry reforming reaction (DR) :-



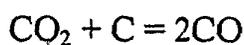
Or by methane cracking :-



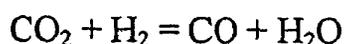
But CO can be supplied by the dry reforming reaction (DR) :-



OR Boudouard reaction :-



OR (RWGS) reaction :-



OR steam reforming reaction :-

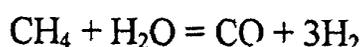


Table (4.2) . Conversion of CO₂ and CH₄ on Rh / γ -Al₂O₃ at the studied conditions .

Temperature	600 °C		700°C		800°C	
Space Velocity ccg ⁻¹ .h ⁻¹	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂
18000	58.47	71.62	67.03	77.63	94.83	93.44
36000	33.96	41.97	46.62	59.49	58.94	66.01
45000	26.01	43.41	30.41	51.05	36.98	56.8
60000	10.79	5.15	16.71	25.06	25.56	37.74

4. 1. 3. Conversion of heavy components :-

4. 1. 3. 1. 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 Fig(4.3-a,4.4-a) because the CO₂- reforming of N.G. is highly endothermic reaction .

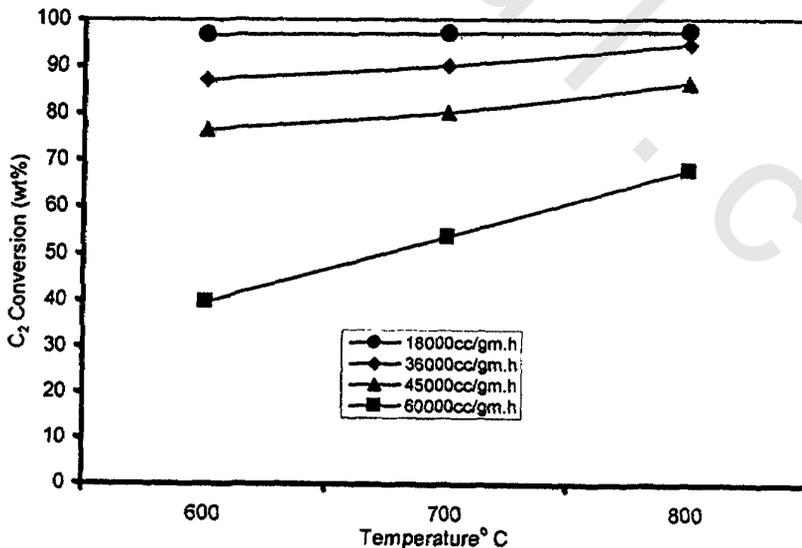


Fig (4.3-a) . Conversion versus temperatures of C₂- alkane on Rh / γ -Al₂O₃ catalyst at different space velocities .

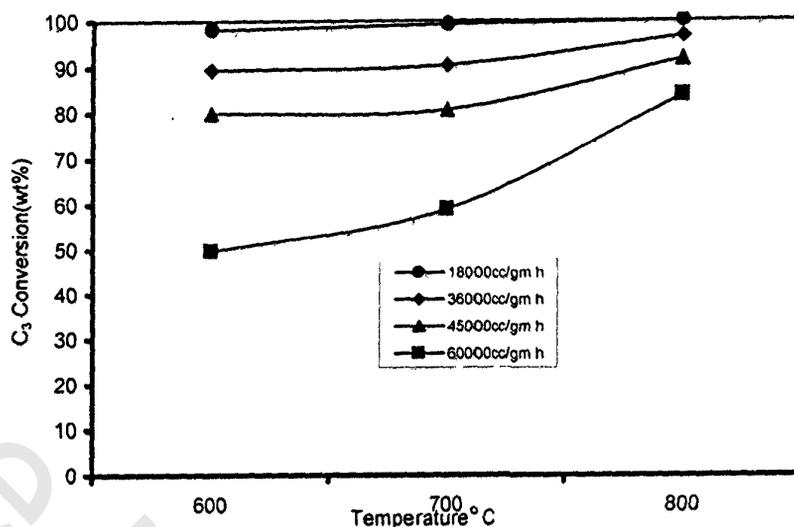


Fig (4.4-a) . Conversion versus temperatures of C₃- alkanes on Rh / γ -Al₂O₃ catalyst at different space velocities .

Also, the conversion of ethane and propane increased with the decreasing of space velocity which is the order of increasing contact time . The highest conversion occurred at space velocity 18000 cc.gm⁻¹h⁻¹ for all the three studied temperatures as shown in Table (4.3) due to the highest contact time which is suitable enough for complete reaction .

Table (4.3) . Conversion of C₂ - and C₃ - alkanes on Rh / γ -Al₂O₃ catalyst at the studied conditions .

Temperature	600 °C		700 °C		800 °C	
	C ₂	C ₃	C ₂	C ₃	C ₂	C ₃
Space Velocity ccg ⁻¹ .h ⁻¹						
18000	96.71	98.13	97.04	99.21	97.38	99.99
36000	87.18	89.5	90.09	90.46	94.54	96.72
45000	76.55	80.04	80.25	80.78	86.32	91.86
60000	39.69	49.69	53.68	59.05	67.82	83.98

At constant temperature the conversion decreased in the sequence of increasing of space velocity .i.e. conversion at 18000 > 36000 > 45000 > 60000 cc. g⁻¹h⁻¹ in the order of contact time decrease , Fig.(4.3-b , 4.4-b).

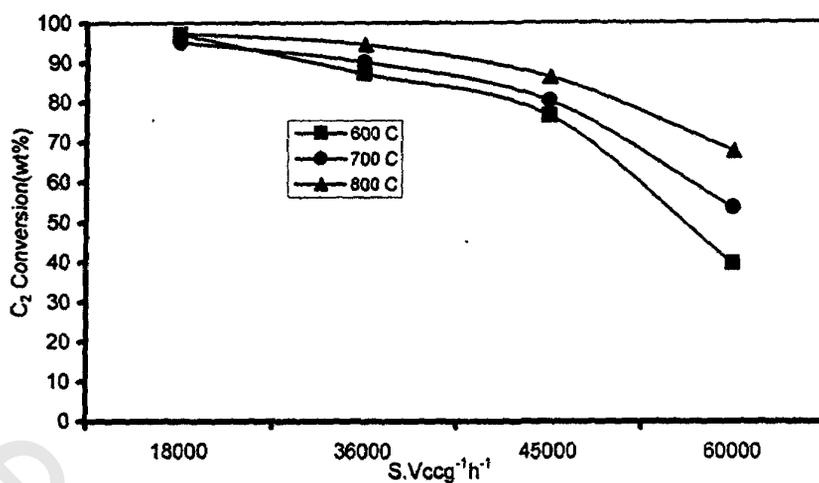


Fig (4.3-b) . Conversion versus space velocities of C₂- alkane on Rh / γ - Al₂O₃ catalyst at different temperatures .

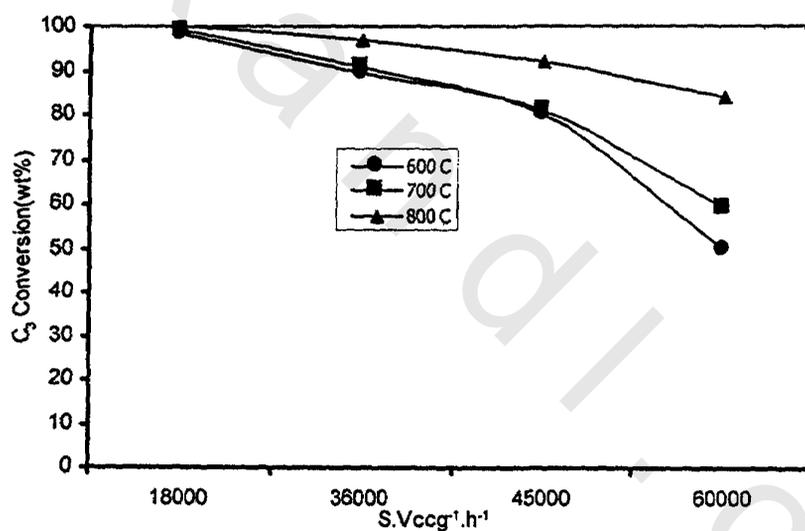


Fig (4.4-b) . Conversion versus space velocities of C₃- alkanes on Rh / γ -Al₂O₃ catalyst at different temperatures .

Generally, the space velocity 18000 cc.gm⁻¹h⁻¹ and the temperature 800°C are the optimum conditions for obtaining the highest conversion percentage of ethane and propane .

4. 1. 3. 2. 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 is dependent on 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⁻¹h⁻¹ exhibited the most efficient velocity for complete conversion of both butanes and heptanes because this velocity offered the suitable enough time for complete reaction .

The temperature 800°C is the preferred one at all the studied space velocities used because the CO₂- reforming of N.G. is highly endothermic reaction , as shown in Fig (4.5 A - C , 4.6 A - C) .

In general , at constant temperature the conversion of butanes (normal and iso-) and pentanes (normal and iso-) was decreased in the sequence of increasing of space velocity .i.e. conversion at 18000 > 36000 > 45000 > 60000 ccg⁻¹h⁻¹ which is the order of decreasing contact time , as given in Table (4.4 , 4.5) . While nearly complete conversion occurred at the temperature 800°C .

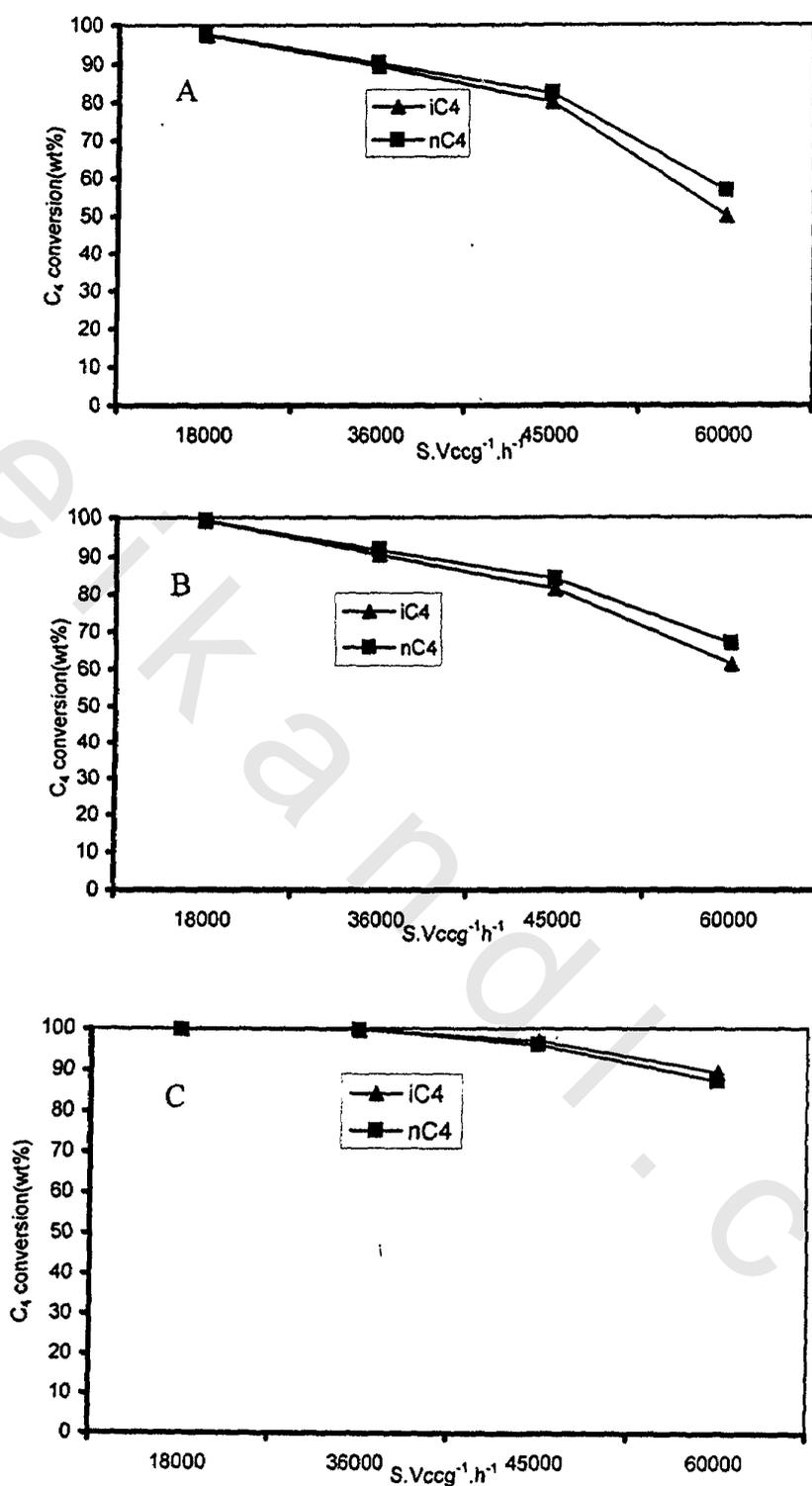


Fig (4.5 A - C) . Conversion versus space velocities of butanes on Rh / γ -Al₂O₃ catalyst at temperatures A (600) , B (700) , C (800) °C .

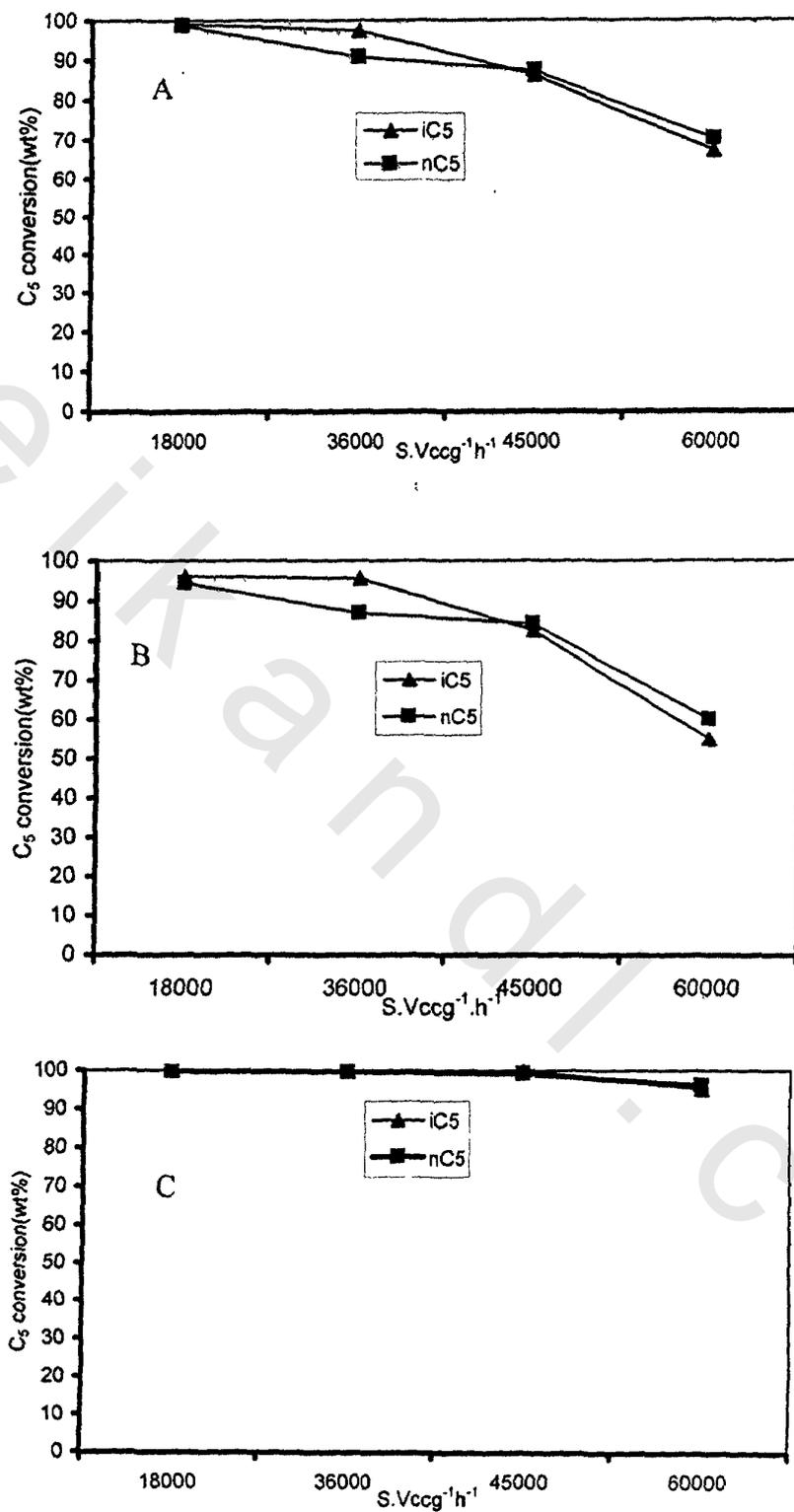


Fig (4.6 . A-C). Conversion versus space velocities of C₅- alkanes on Rh / γ -Al₂O₃ catalyst at temperatures A (600) , B (700) , C (800) °C .

Table (4.4) . Conversion of *i*-C₄ - and *n*-C₄ - alkanes on Rh / γ -Al₂O₃ catalyst at the studied conditions .

Temperature	600 °C		700°C		800°C	
Space Velocity ccg ⁻¹ .h ⁻¹	<i>i</i> -C ₄	<i>n</i> -C ₄	<i>i</i> -C ₄	<i>n</i> -C ₄	<i>i</i> -C ₄	<i>n</i> -C ₄
18000	97.41	97.61	99.26	99.08	99.99	99.89
36000	89.52	90.25	90.55	91.7	99.96	99.7
45000	80.1	82.46	81.53	84.25	96.97	96.03
60000	49.87	56.54	61.47	67.01	89.3	87.22

It is clear that at the temperature 800°C for *n*-C₅ and *i*-C₅ complete conversion occurred at all the studied space velocities as shown in Fig (4.5 A – C , 4.6 A – C) and given in Table (4.5) .

Table (4.5) . Conversion of *i*-C₅ - and *n*-C₅ - alkanes on Rh / γ -Al₂O₃ catalyst at the studied conditions .

Temperature	600 °C		700°C		800°C	
Space Velocity ccg ⁻¹ .h ⁻¹	<i>i</i> -C ₅	<i>n</i> -C ₅	<i>i</i> -C ₅	<i>n</i> -C ₅	<i>i</i> -C ₅	<i>n</i> -C ₅
18000	96.2	94.46	99.16	98.73	99.96	99.79
36000	95.62	86.96	97.45	90.77	99.87	99.75
45000	82.63	84.28	86.23	87.38	99.96	99.18
60000	54.89	59.96	67.2	70.19	95.21	96.2

Generally , the space velocity 18000 cc.gm⁻¹.h⁻¹ and the temperature 800°C are the optimum condition for obtaining the highest conversion percentage of butanes (normal and iso-) and pentanes (normal and iso-) .

4. 1. 3. 3. Hexanes and heptanes conversion :-

The hexanes and heptanes components exhibit conversion under all working conditions (space velocity and temperature) but at different rates .

Generally the best conversion of hexanes and heptanes was obtained at the optimum conditions, space velocity 18000 cc.g⁻¹.h⁻¹ and temperature 800°C, as given in Fig (4.7,4.8) .

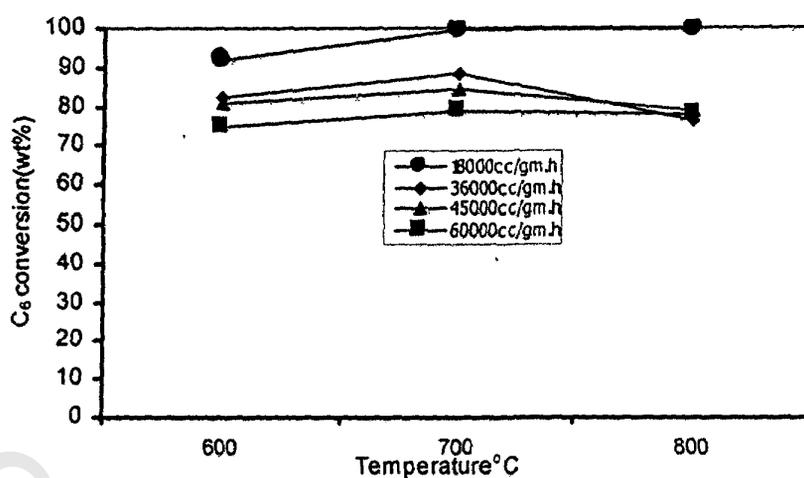


Fig (4.7) . Conversion versus temperatures of C₆ - alkanes on Rh / γ -Al₂O₃ catalyst at different space velocities .

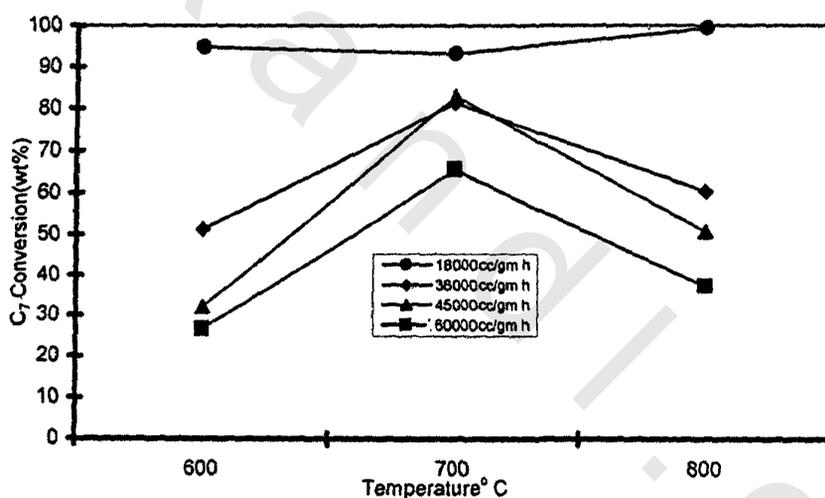


Fig (4.8) . Conversion versus temperatures of C₇ - alkanes on Rh / γ -Al₂O₃ catalyst at different space velocities .

At space velocities 36000 , 45000 and 60000 cc.g⁻¹.h⁻¹, conversion was obtained at all the studied temperatures but the temperature 700°C gives the highest conversion than, as shown in Fig (4.7 , 4.8) and given in Table (4.6).

Table (4.6) . Conversion of C_6^+ - and C_7^+ - alkanes on Rh / γ - Al_2O_3 catalyst at the studied conditions .

Temperature Space Velocity $ccg^{-1}.h^{-1}$	600 °C		700°C		800°C	
	C_6^+	C_7^+	C_6^+	C_7^+	C_6^+	C_7^+
18000	92	94.77	99.25	93.12	99.29	99.09
36000	82.1	51.28	88.45	81.3	76.12	60.4
45000	80.87	32.07	84.25	82.98	78.72	50.82
60000	74.69	26.6	78.65	65.55	77.84	37.4

4.1.4. Formation of syngas (H_2 and CO) :-

H_2 and CO Selectivity:-

The selectivity reflects the actual behavior of the studied three catalysts under the working conditions . It varies with metal type , temperature , and space velocity . Therefore it should be referred to specified reaction conditions (Paturza et al ;2003) .

The H_2 and CO selectivity using Rh / γ - Al_2O_3 catalyst at different conditions are given in Table (4.7) .

It has been found that the selectivity of both H_2 and 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 .

Table(4.7) . H_2 and CO selectivity on Rh / γ - Al_2O_3 catalyst at different temperatures and space velocities .

Temperature Space Velocity $ccg^{-1}.h^{-1}$	600°C		700°C		800°C	
	$H_2\%$	CO%	$H_2\%$	CO%	$H_2\%$	CO%
18000	22	42.62	30.86	52.63	36.26	58.12
36000	22	36.93	26.17	40.05	29.87	47.86
45000	6.17	31.97	13.36	34.02	17.61	44.21
60000	3.63	13.48	7.44	22.65	8.88	32.67

The Rh / γ -Al₂O₃ selectivity with respect to H₂ and CO was achieved maximally at temperature of 800°C and space velocity 18000ccg⁻¹h⁻¹.

As shown in Table (4.7) Rh / γ -Al₂O₃ catalyst showed good selectivity to hydrogen at the smaller velocities , for the higher reaction temperature , where the reverse water gas shift reaction did not take place significantly for reaction temperature above 600°C .

In general ; H₂ / CO ratio < 1 in agreement with Zhang et al (1996) , as given in Table(4.8) . CO selectivity was always higher than H₂ selectivity, and this aspect can be explained considering that CO is also produced from other chemical reactions (Portugal et al ;2000) , (Bhat et al ; 1997) and (Mark et al ; 1996) .

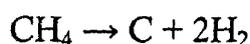
Table (4.8) . H₂ / CO ratio on Rh / γ -Al₂O₃ catalyst at different temperatures and space velocities .

Temperature	600°C	700°C	800°C
Space Velocity ccg ⁻¹ h ⁻¹	H ₂ / CO		
18000	0.51	0.59	0.62
36000	0.6	0.65	0.64
45000	0.27	0.39	0.4
60000	0.19	0.33	0.27

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



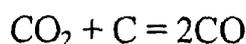
Or by methane cracking:-



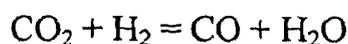
But CO can be supplied by the dry reforming reaction (DR):-



OR Boudouard reaction:-



OR (RWGS) reaction:-



OR steam reforming reaction:-

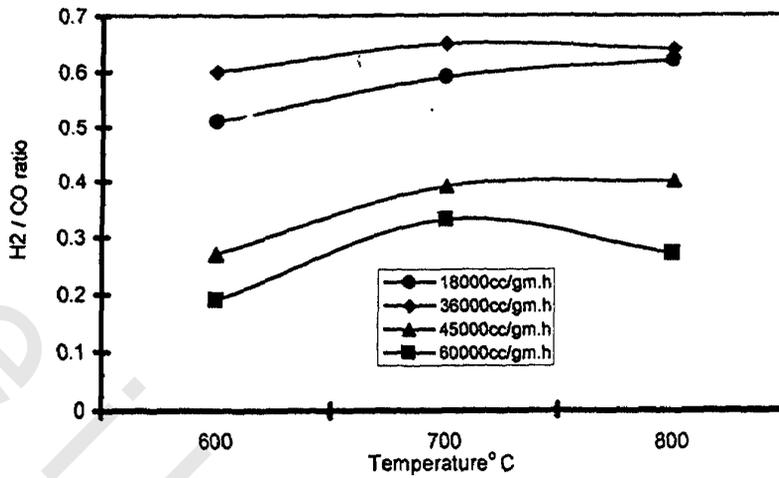
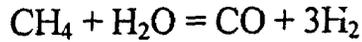


Fig. (4.9.a) . H₂ / CO ratio versus temperatures on Rh / γ -Al₂O₃ catalyst at different space velocities .

Fig.(4.9.a) shows that at constant temperature ; H₂ / CO ratio increased in the order of 36000 > 18000 > 45000 > 60000 cc.g⁻¹.h⁻¹ , H₂ / CO ratio is below 1.0 in all cases .

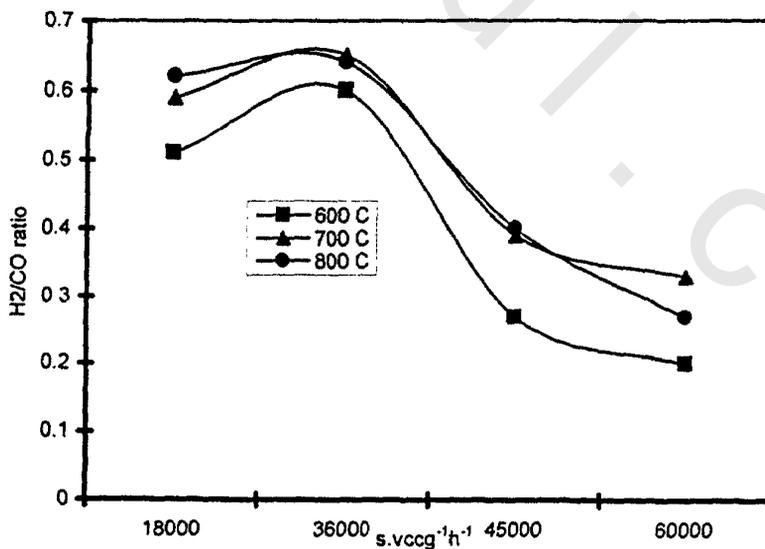


Fig. (4.9.b) . H₂ / CO ratio versus space velocities on Rh / γ -Al₂O₃ catalyst at different temperatures .

The maximum H₂ /CO ratio of Rh / γ -Al₂O₃ was achieved at temperature of 700°C and space velocity 36000ccg⁻¹h⁻¹ Fig.(4.9.a,b) .

4.2. Ru / γ - Al₂O₃ catalyst :-

4.2.1. CH₄ conversion :-

The 0.5 % Ru /Al₂O₃ 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 CO₂ reforming reaction is a highly endothermic reaction (Yokota et al ; 2002) :-



At constant space velocity CH₄ conversion increased as the temperatures increased from 600°C to 800°C as shown in Fig. (4.10-a) .

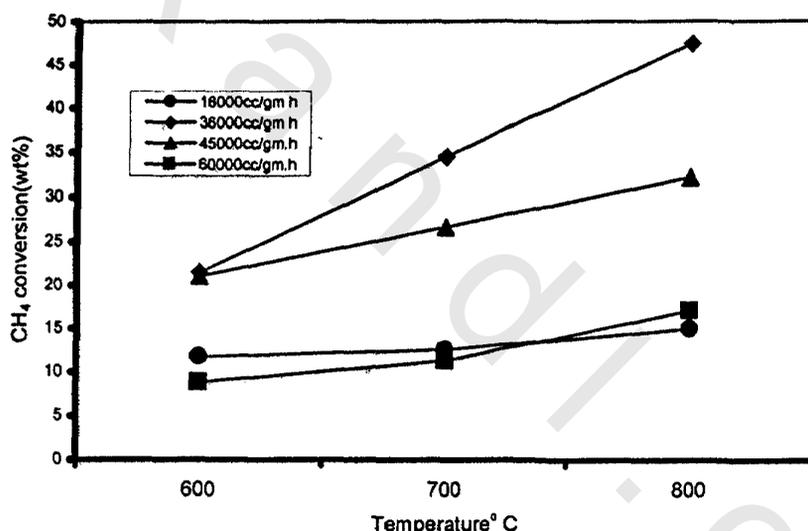


Fig. (4.10.a) . Conversion versus temperatures of CH₄ on Ru / γ -Al₂O₃ catalyst at different space velocities .

At constant temperature, CH₄ conversion increased in the order of 36000 > 45000 > 60000 > 18000 ccg⁻¹h⁻¹; as shown in Fig. (4.10-b) , and given in Table (4. 9) .

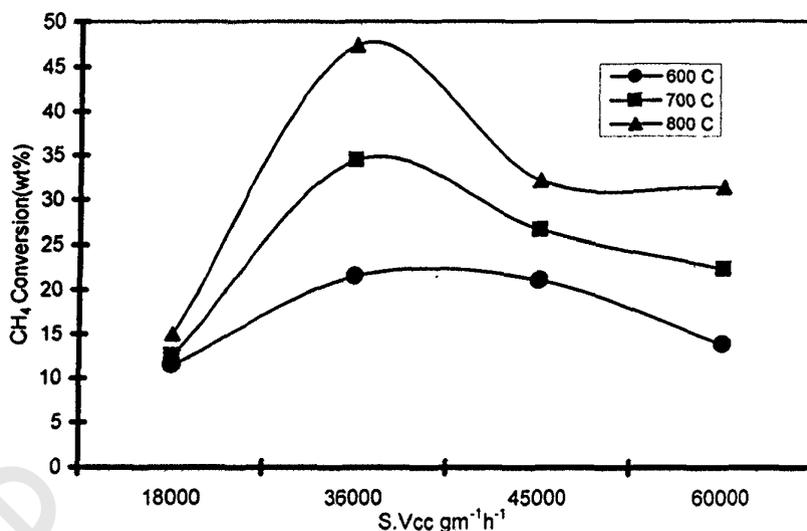


Fig. (4.10-b) . Conversion versus space velocities of CH₄ on Ru / γ -Al₂O₃ catalyst at different temperatures .

However ; the 0.5% Ru / γ -Al₂O₃ conversion with respect to CH₄ was achieved maximally at temperature of 800°C and space velocity 36000 cc g⁻¹ h⁻¹; as shown in Fig.(4.10 a , b) and the data given in Table (4.9) .

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 (Ferreira-Aparicio et al ; 1998) .

The activity of these catalysts can be correlated with the accessible metal surface area ; an increase in metal surface area i.e., the number of active sites, leads to an increase in CH₄ conversion (Tsipouriari et al ; 1994) .

The increase of conversion with decreasing space velocity from 60000 cc g⁻¹h⁻¹ to 36000 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) .

4.2.2. CO₂ Conversion:-

The 0.5 % Ru /Al₂O₃ catalyst exhibited reactivity with varying degrees within the whole temperature range .

At constant flow rate, the activity of catalyst toward CO₂ conversion was increased as temperature increased from 600°C to 800°C as shown in Fig. (4.11-a) . This occurs because CO₂ reforming reaction is a highly endothermic reaction (Yokota et al ; 2002) .

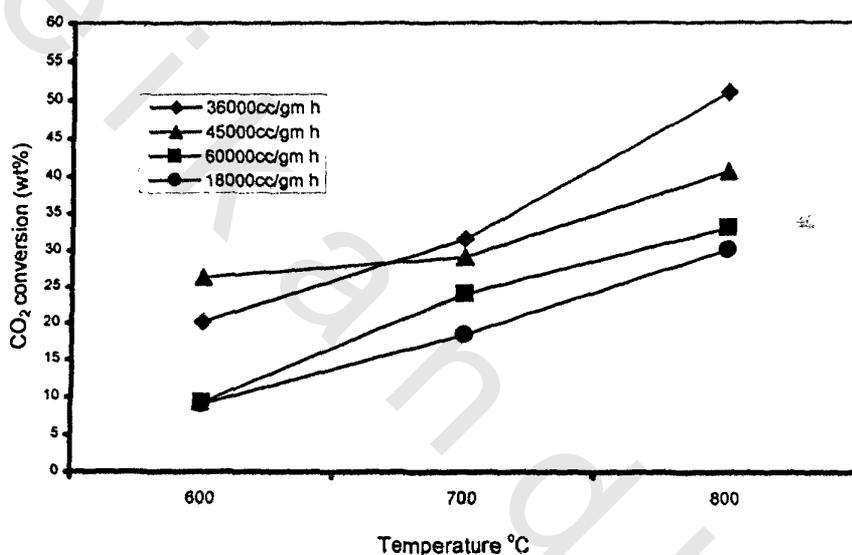


Fig. (4.11-a) . CO₂ Conversion versus temperatures on Ru / γ -Al₂O₃ catalyst at different space velocities .

For 700°C and 800°C temperatures , CO₂ conversion increased in the order of 36000 > 45000 > 60000 > 18000 ccg⁻¹h⁻¹ ; while at 600°C the maximum conversion was shifted to a higher space velocity (45000 ccg⁻¹h⁻¹) as shown in Fig (4.11-b) and the data given in Table (4.9) .

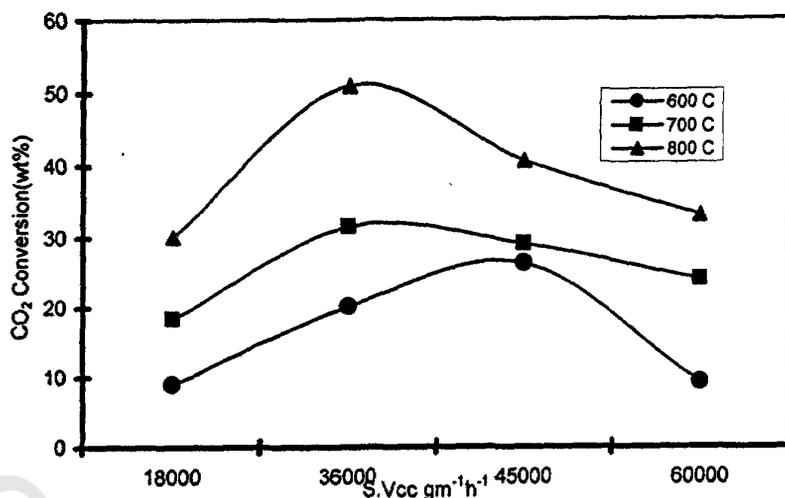


Fig. (4.11-b) . Conversion versus space velocities of CO₂ on Ru / γ -Al₂O₃ catalyst at different temperatures .

However ; the 0.5 % Ru / Al₂O₃ conversion with respect to CO₂ was achieved maximally at temperature of 800°C and space velocity 36000 cc g⁻¹h⁻¹; as shown in Fig.(4.11- a , b) and the data given in Table (4.9) .

As given in Table (4.9) the conversion of CO₂ was always higher than the conversion of CH₄ , at the same conditions although a feed ratio of unity was used ; in agreement with Zhang et al ; (1996) for example , for Ru / γ -Al₂O₃ catalyst at space velocity = 18000 ccg⁻¹h⁻¹ & 800°C , CH₄ conversion was 15 % , while , CO₂ conversion was 30.09 % this occur due to RWGS (reverse water gas shift reaction) :-



Table (4.9) . Conversion of CO₂ and CH₄ on Ru / γ -Al₂O₃ at the studied conditions .

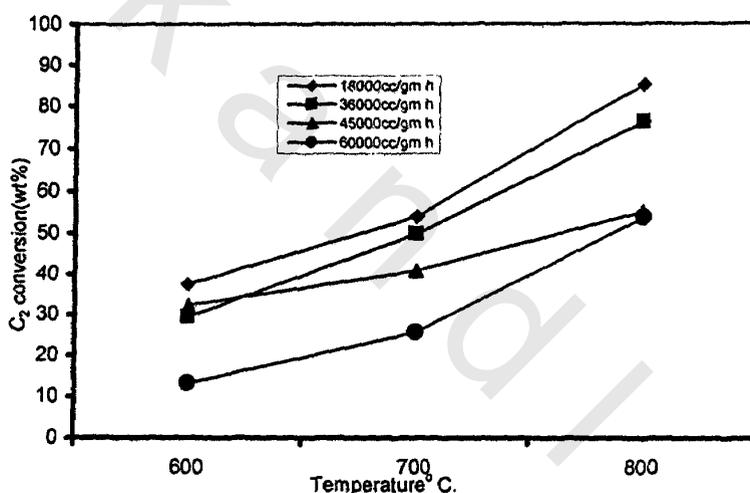
Temperature	600 °C		700°C		800°C	
	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂
Space Velocity ccg ⁻¹ .h ⁻¹						
18000	11.74	8.96	12.56	18.38	15	30.09
36000	21.5	20.13	34.46	31.54	47.42	50.95
45000	21.05	26.31	26.62	29.05	32.17	40.65
60000	8.83	9.17	11.28	23.99	17.1	33.08

There are different pathways to CO₂ to be consumed so its conversion is usually higher than CH₄ conversion , (Portugal et al ;2000) , (Bhat et al ; 1997) and (Mark et al ; 1996) .

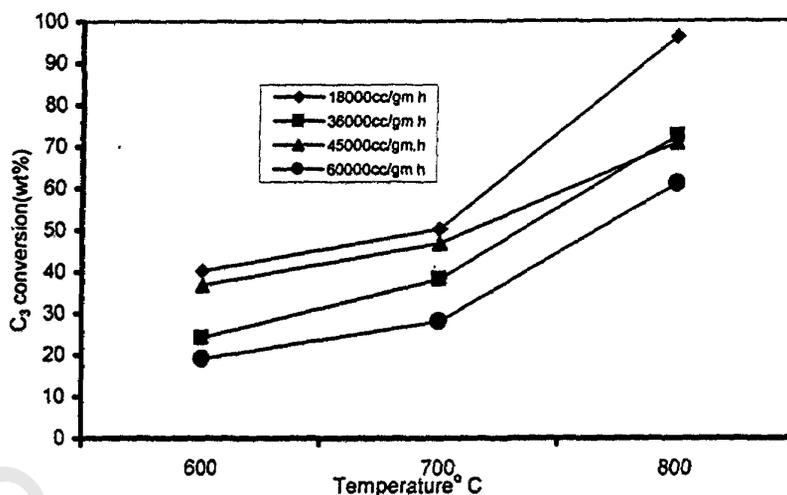
4. 2. 3. Conversion of heavy components :-

4. 2. 3. 1. 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 Fig (4.12.a , 4.13.a) because the CO₂ - reforming of N.G. is a highly endothermic reaction .

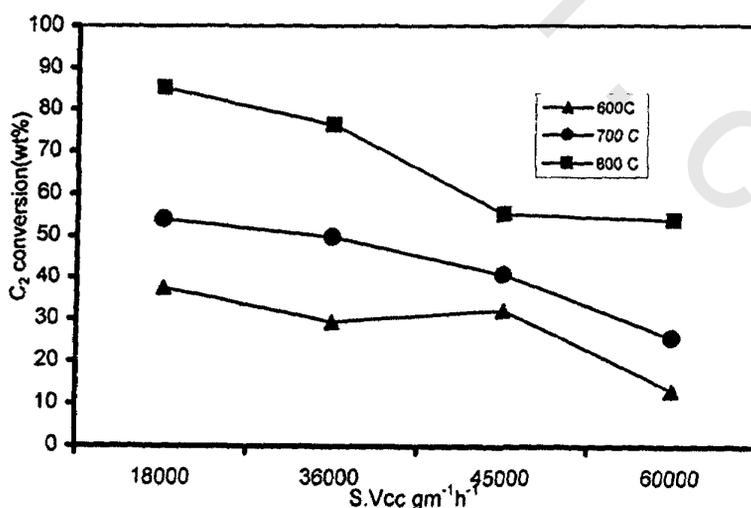


Fig(4.12.a) . Conversion versus temperatures of C₂ - alkane on Ru / γ-Al₂O₃ catalyst at different space velocities .



Fig(4.13.a) . Conversion versus temperatures of C₃ - alkane on Ru / γ -Al₂O₃ catalyst at different space velocities .

At constant temperature ; the conversion C₂ 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 C₃ the sequence was slightly different 18000 > 45000 > 36000 > 60000 ccg⁻¹h⁻¹ at the temperature 600°C & 700°C , as shown in Fig (4.12 . b , 4.13 . b) , and Table (4.10) .



Fig(4.12.b) . Conversion versus space velocities of C₂- alkane on Ru / γ -Al₂O₃ catalyst at different temperatures .

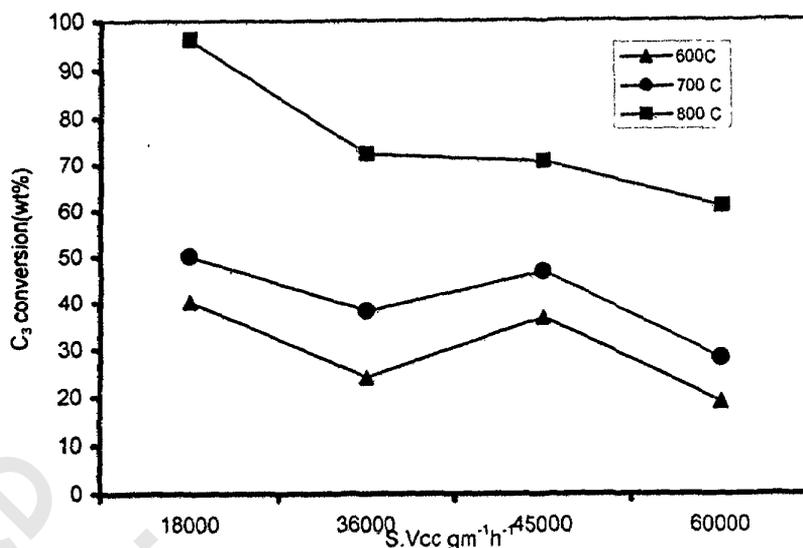


Fig (4.13.b) . Conversion versus space velocities of C₃ - alkanes on Ru / γ - Al₂O₃ catalyst at different temperatures .

Generally, the space velocity 18000 ccg⁻¹h⁻¹ and the temperature 800°C are the optimum conditions for obtaining the highest conversion percentage of ethane and propane .

Table (4.10) . Conversion of C₂ - and C₃ – alkanes on Ru / γ -Al₂O₃ catalyst at the studied conditions .

Temperature	600 °C		700°C		800°C	
	C ₂	C ₃	C ₂	C ₃	C ₂	C ₃
Space Velocity ccg ⁻¹ .h ⁻¹						
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

4. 2. 3. 2. 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 $18000 \text{ ccg}^{-1}\text{h}^{-1}$ exhibited the most efficient velocity for complete conversion of both butanes and heptanes because this velocity offered the suitable enough time for complete reaction .

The temperature 800°C is the preferred one at all the studied space velocities used because the CO_2 - reforming of N.G. is highly endothermic reaction , as shown in Fig (4.14 .A-C , 4.15 .A-C) .

It is clear that the temperature 800°C 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 Fig (4.13.A-C , 4.14.A-C) .

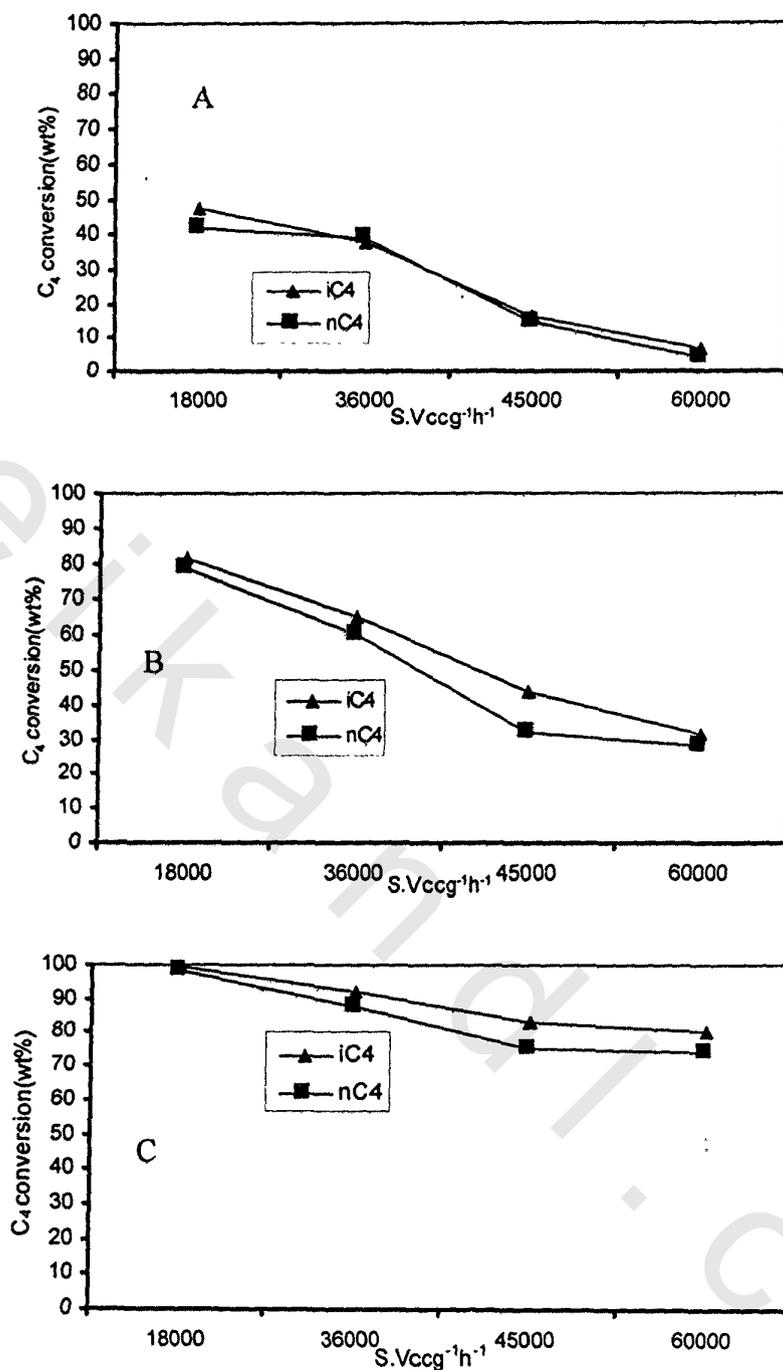


Fig (4.14A-C) . Conversion versus space velocities of C₄ – alkanes on Ru / γ -Al₂O₃ catalyst at A (600) , B (700) , C (800) °C .

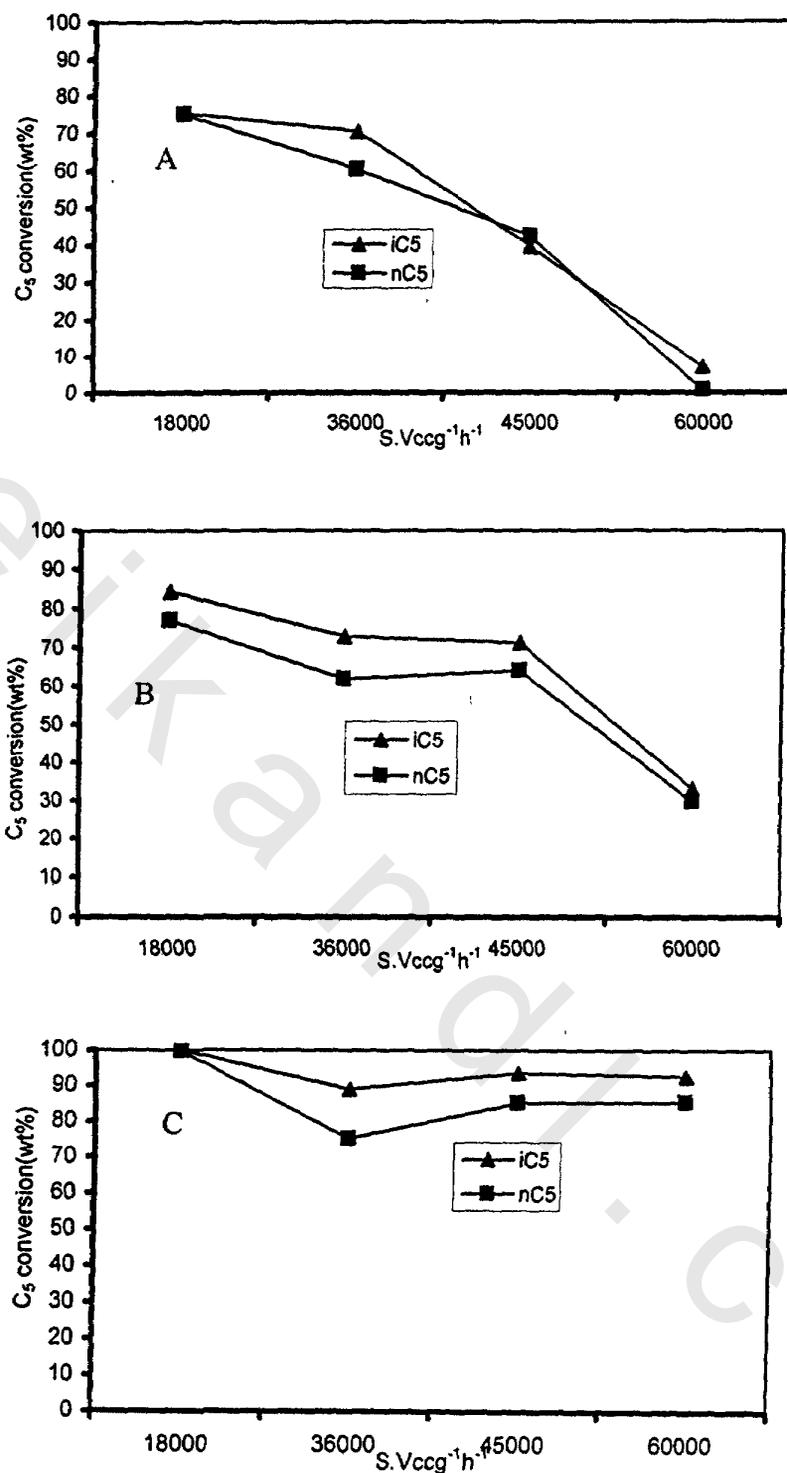


Fig (4.15 . A-C) . Conversion versus space velocities of C₅ – alkanes on Ru / Al₂O₃ catalyst at temperatures A (600) , B (700) , C (800) °C .

At 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⁻¹h⁻¹ in the order of decreasing the contact time, as shown in Fig.(4.14.A-C , 4.15.A , B) . However ; the decrease in conversion with increasing space velocity was not very pronounced for pentanes at 800°C Fig.(4.15.C) and the data given in Tables (4.11 , 4.12) .

Table (4.11) . Conversion of *i*-C₄- and *n*-C₄- alkanes on Ru / γ -Al₂O₃ catalyst at the studied conditions.

Temperature	600 °C		700°C		800°C	
Space Velocity ccg ⁻¹ .h ⁻¹	<i>i</i> -C ₄	<i>n</i> -C ₄	<i>i</i> -C ₄	<i>n</i> -C ₄	<i>i</i> -C ₄	<i>n</i> -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

Also, at the four different space velocities the conversion of iso-butanenes and iso-pentanenes was generally higher than *n*- butanenes and *n*- pentanenes conversion at all temperatures Table (4.11 , 4.12) , this may be occur because the iso-components are more active due to the branching in the chain .

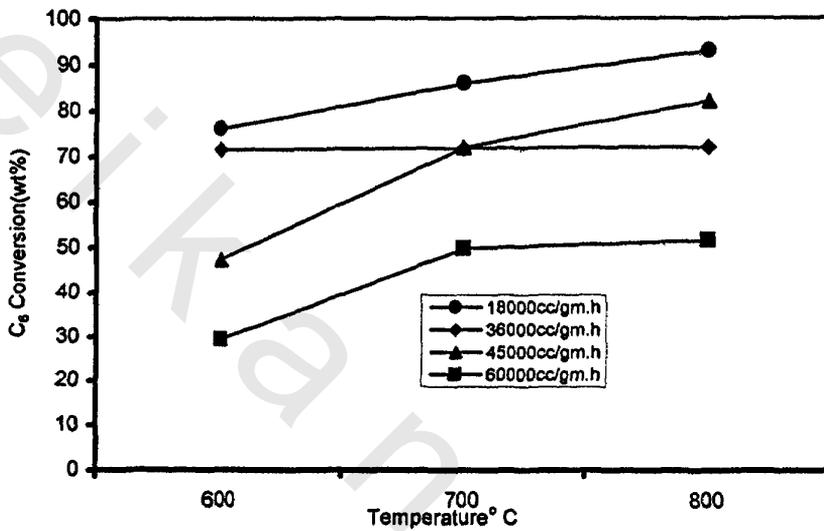
Table (4.12) . Conversion of *i*-C₅- and *n*-C₅- alkanes on Ru / γ - Al₂O₃ catalyst at the studied conditions .

Temperature	600 °C		700°C		800°C	
Space Velocity ccg ⁻¹ .h ⁻¹	<i>i</i> -C ₅	<i>n</i> -C ₅	<i>i</i> -C ₅	<i>n</i> -C ₅	<i>i</i> -C ₅	<i>n</i> -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

Generally, the space velocity 18000 ccg⁻¹h⁻¹ and the temperature 800°C are the optimum condition for obtaining the highest conversion percentage of the butanenes (normal and iso-) and pentanenes(normal and iso-) .

4. 2. 3. 3. Hexanes and heptanes conversion :-

The conversion of hexanes and heptanes increased with increasing the temperature, 800°C is the most efficient degree giving high conversion percentage as shown in Fig (4.16 , 4.17) because the CO₂ - reforming of N.G. is highly endothermic reaction .



Fig(4.16) . Conversion versus temperatures of C₆ – alkanes on Ru / γ -Al₂O₃ catalyst at different space velocities .

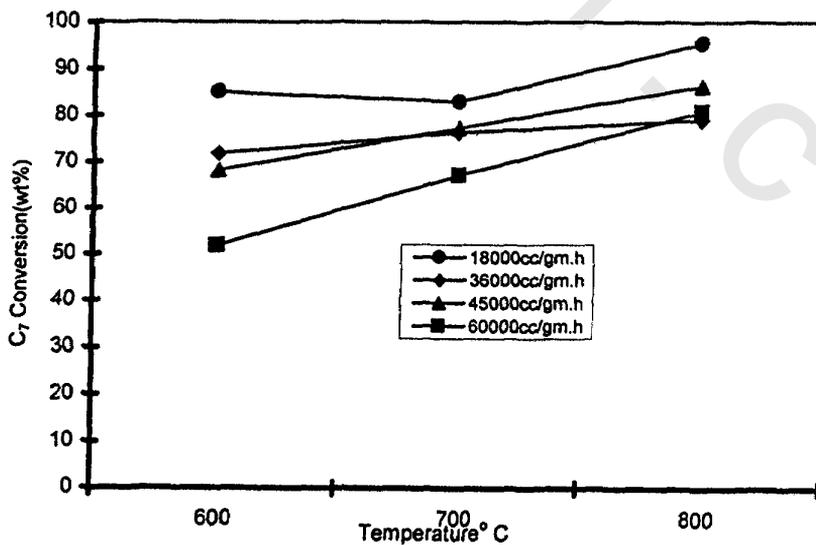


Fig (4.17) . Conversion versus temperatures of C₇– alkanes on Ru / γ -Al₂O₃ catalyst at different space velocities .

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 (4.13) .

Table (4.13) . Conversion of C₆⁺- and C₇⁺- alkanes on Ru / γ -Al₂O₃ catalyst at the studied conditions .

Temperature	600 °C		700°C		800°C	
	C ₆ ⁺	C ₇ ⁺	C ₆ ⁺	C ₇ ⁺	C ₆ ⁺	C ₇ ⁺
Space Velocity ccg ⁻¹ .h ⁻¹						
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

Generally, the space velocity 18000 ccg⁻¹.h⁻¹ and the temperature 800°C are the optimum condition for obtaining the highest conversion percentage of the hexanes and heptanes .

4. 2. 4. Formation of syngas (H₂ and CO) :-

The H₂ and CO selectivity using Ru / γ -Al₂O₃ catalyst at different conditions are given in Table (4.14) .

It has been found that the selectivity of both H₂ and CO increased as a function of temperature for all the studied velocities. Also ; at constant temperature the selectivity of both H₂ and CO decreased with increasing the space velocity .

However ; no hydrogen was present at 45000 , 60000 ccg⁻¹.h⁻¹ for the 3 - tested temperatures , but CO was always detected at the different conditions as given in Table(4.14) . Only Ru / γ -Al₂O₃ catalysts showed

good selectivity to H₂ and CO at 18000 , 36000 cc.g⁻¹.h⁻¹ for space velocities examined , at 800°C reaction temperature .

Generally ; H₂ / CO ratio < 1 is observed due to the higher CO selectivity than H₂ selectivity , in agreement with (Wang et al ; 2000) ; as given in Table (4.15) this aspect can be explained by considering that CO is also formed as a product in other chemical reactions (Portugal et al ; 2000) , (Bhat et al ; 1997) and (Mark et al ; 1996) . Hydrogen produced as a result of the reforming reaction could be consumed by the RWGS which is more active at lower temperature (Wang et al ; 2000) .

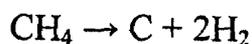
Table (4.14) . H₂ and CO selectivity on Ru / γ-Al₂O₃ catalyst at different temperatures and space velocities .

Temperature Space Velocity ccg ⁻¹ .h ⁻¹	600°C		700°C		800°C	
	H ₂ %	CO%	H ₂ %	CO%	H ₂ %	CO%
18000	0	0.91	0	1.48	5.31	14.28
36000	0	0.72	0	1.07	2.54	7.82
45000	0	0.56	0	0.66	0	5.98
60000	0	0.22	0	0.42	0	5.22

The hydrogen can be supplied by the dry reforming reaction (DR) :-



Or by methane cracking:-



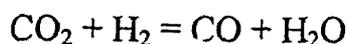
But CO can be supplied by the dry reforming reaction (DR) :-



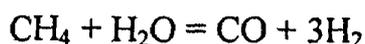
OR Boudouard reaction:-



OR (RWGS) reaction:-



OR steam reforming reaction:-



Generally , the space velocity $18000\text{ccg}^{-1}\text{h}^{-1}$ and the temperature 800°C are the optimum conditions for obtaining the highest selectivity for H_2 and CO individually .

On the other hand ; the best conditions to produce a high ratio of H_2 / CO (0.372) is $36000\text{ccg}^{-1}\text{h}^{-1}$ space velocity as shown in Fig (4.18.b) , and 800°C for temperature as shown in Fig (4.18.a) , and the data given in Table (4.15).

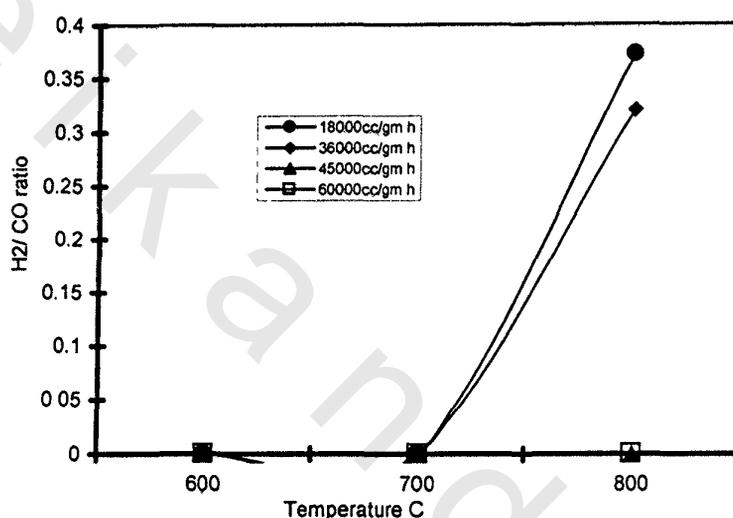


Fig.(4.18.a) . H_2 / CO ratio versus temperatures on $\text{Ru} / \gamma\text{-Al}_2\text{O}_3$ catalyst at different space velocities .

Table (4.15) . H_2 / CO ratio on $\text{Ru} / \gamma\text{-Al}_2\text{O}_3$ catalyst at different temperatures and space velocities .

Temperature	600°C	700°C	800°C
Space Velocity $\text{ccg}^{-1}\text{h}^{-1}$	H_2 / CO		
18000	0	0	0.372
36000	0	0	0.32
45000	0	0	0
60000	0	0	0

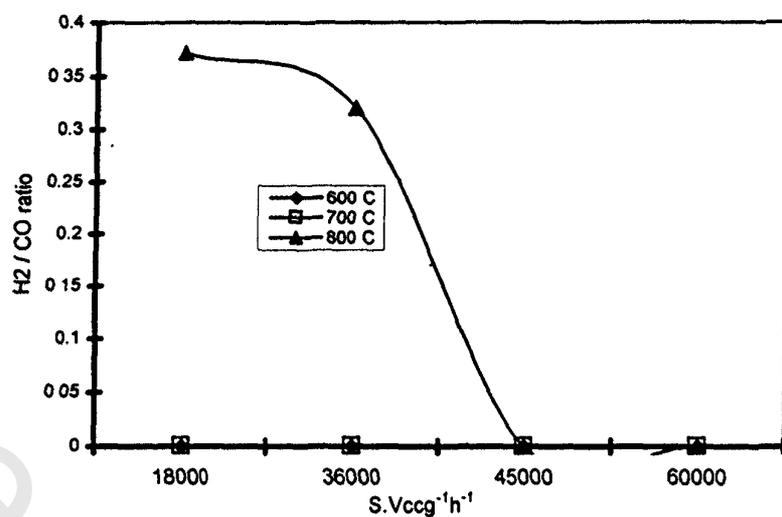


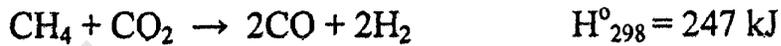
Fig (4.18.b) . H₂ / CO ratio versus space velocities on Ru / γ -Al₂O₃ catalyst different temperatures .

4.3. Ir / γ -Al₂O₃ catalyst :-

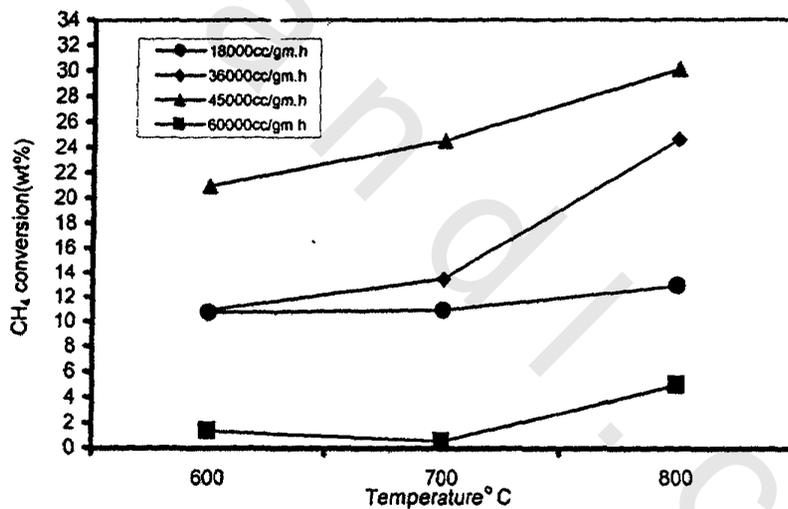
4.3.1. CH₄ Conversion :-

The 0.5 % Ir / γ -Al₂O₃ catalyst exhibit reactivity with varying degrees within the whole temperature range .

At constant flow rate, the activity of the catalyst increased as temperature increased ,This occurs because CO₂ reforming reaction is a highly endothermic reaction (Yokota et al ; 2002) :-



At constant space velocities CH₄ conversion increased as the temperature increased from 600°C to 800°C as shown in Fig. (4.19.a) .

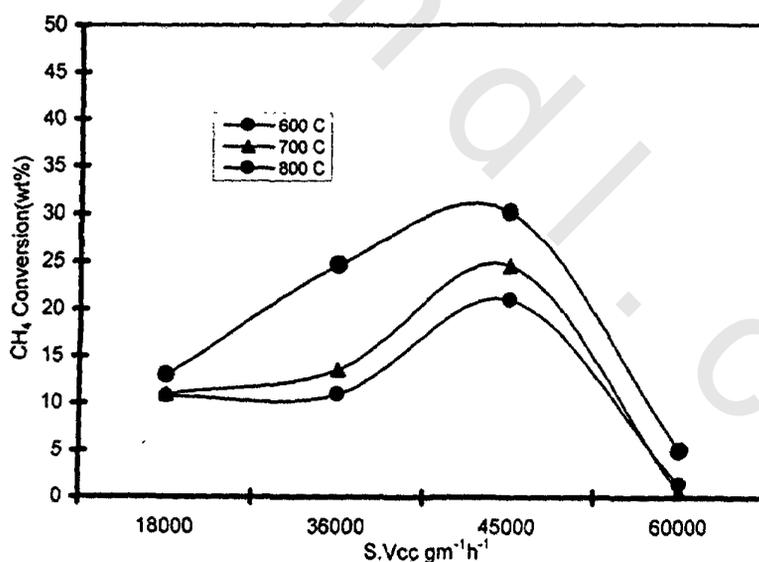


Fig(4.19.a) . Conversion versus temperatures of CH₄ on Ir / γ -Al₂O₃ catalyst at different space velocities .

Ir - based catalysts are stable at high temperature 800°C , due to their high resistance towards carbon deposition under reaction conditions ; when decreasing the temperature high deactivation rates are observed by accumulation of carbon on the Ir-surface probably this deactivation takes place as a result of an easier methane activation as compared with that of CO₂ (Ferreira - Aparicio et al ;1998) .

At constant temperature , CH_4 conversion increase with increasing space velocity reaches a maximum at $45000 \text{ ccg}^{-1} \cdot \text{h}^{-1}$ then decreases ; as shown in Fig (4.19.b) , Table (4.16) .

This may be related to formation of CH_x fragments , their reactivity and their amount , ability of catalyst to insert them in the reaction . All these factors contribute to determine the optimized conditions for reaction (Ferreira - Aparicio et al ; 1998) .The activity of these catalysts can be correlated with the accessible metal surface area . Increasing the flow rate allows the reacting species to reach more metal active sites . An increase in metal surface area ; i.e , the number of active sites , leads to an increase in CH_4 conversion (Mark et al ; 1996) .



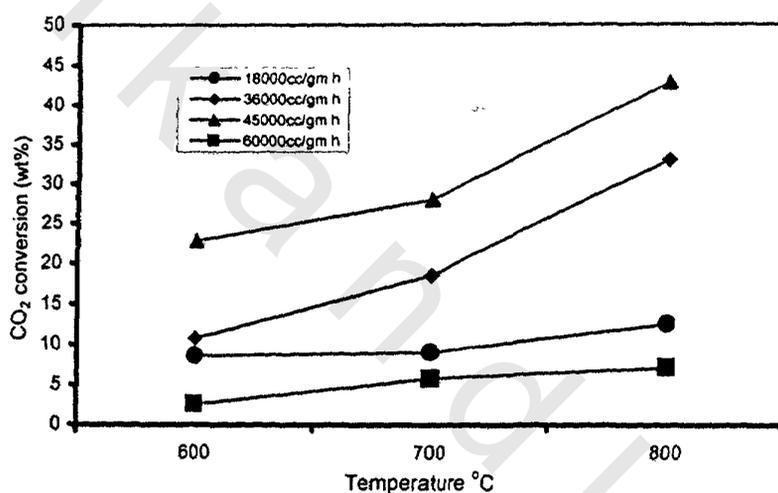
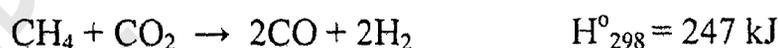
Fig(4.19.b) . Conversion versus space velocities of CH_4 on Ir / $\gamma\text{-Al}_2\text{O}_3$ catalyst at temperatures .

However ; the 0.5% Ir / Al_2O_3 conversion with respect to CH_4 was achieved maximally at a temperature of 800°C and a space velocity of $45000 \text{ ccg}^{-1} \cdot \text{h}^{-1}$; as shown in Fig.(4.19 a , b) and given in Table (4.16) .

4.3.2. CO₂ Conversion :-

The 0.5 % Ir/Al₂O₃ catalyst exhibits reactivity towards CO₂ conversion with varying degrees within the whole temperature range .

At constant flow rate, the activity of catalyst toward CO₂ conversion increased as temperature increased from 600°C to 800°C as shown in Fig. (4.20.a) . This occurs because CO₂ reforming reaction is a highly endothermic reaction (Yokota et al ; 2002) :-



Fig(4.20.a) . Conversion versus temperatures of CO₂ on Ir / γ-Al₂O₃ catalyst at different space velocities .

The observed behavior is in agreement with that reported by Ferreira - Aparicio et al (1998) . These others argued that Ir-based catalysts are stable at high temperature 800°C, due to their high resistance towards carbon deposition under reaction conditions ; when decreasing temperature high deactivation rates are observed by accumulation of carbon on the Ir-surface probably this deactivation takes place as a result of an easier methane activation as compared with that of CO₂ .

Similar to the case of CH₄ conversion at constant temperature , CO₂ - conversion increase in the order of 45000 > 36000 > 18000 > 60000 ccg⁻¹.h⁻¹ ; as shown in Fig (4.20.b) .

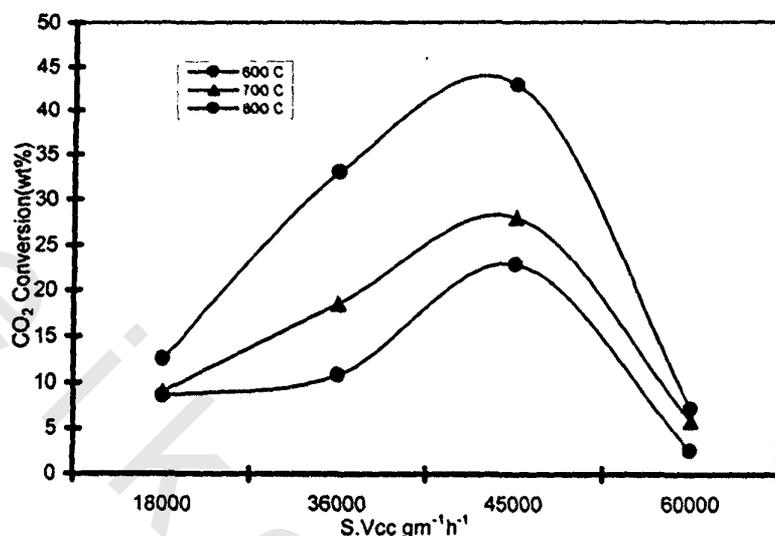


Fig (4.20.b) . Conversion versus space velocities of CO₂ on Ir / γ -Al₂O₃ catalyst at different temperatures .

However ; the 0.5 % Ir /Al₂O₃ conversion with respect to CO₂ was achieved maximally at temperature of 800°C and space velocity 45000ccg¹h⁻¹; as shown in Fig. (4.20-a,b) and given in Table (4.16) .

The conversion of CO₂ was always higher than the conversion of CH₄ , under the same conditions although a feed ratio of unity was used , in agreement with (Zhang et al ; 1996) , as given in Table (4.16) , for example , for Ir / γ -Al₂O₃ catalyst at space velocity = 45000 ccg⁻¹h⁻¹ , 800°C , CH₄ conversion was 30.11% ,while , CO₂ conversion was 42.88 % this may occur due to RWGS (reverse water gas shift reaction) :-

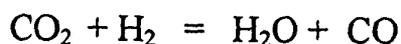


Table (4.16) . Comparison of conversion for CO₂ and CH₄ on Ir / γ-Al₂O₃ at the studied conditions .

Temperature Space Velocity ccg ⁻¹ .h ⁻¹	600 °C		700°C		800°C	
	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂
18000	10.74	8.57	10.96	9.01	12.98	12.52
36000	10.95	10.78	13.56	18.49	24.63	32.99
45000	20.97	22.75	24.56	27.98	30.11	42.88
60000	1.37	2.57	0.54	5.78	4.97	7.11

(i.e) there are different pathways to CO₂ to be consumed so its conversion is usually higher than CH₄ conversion in agreement with Portugal et al (2000) , Bhat et al (1997) and Mark et al (1996) .

4. 3. 3. Conversion of heavy components:-

4. 3. 3. 1. Ethane and propane conversion:-

The conversion of ethane and propane increases with increasing the temperature , 800°C is the most efficient degree giving high conversion percentage as shown in Fig (4.21.a,4.22.a) .

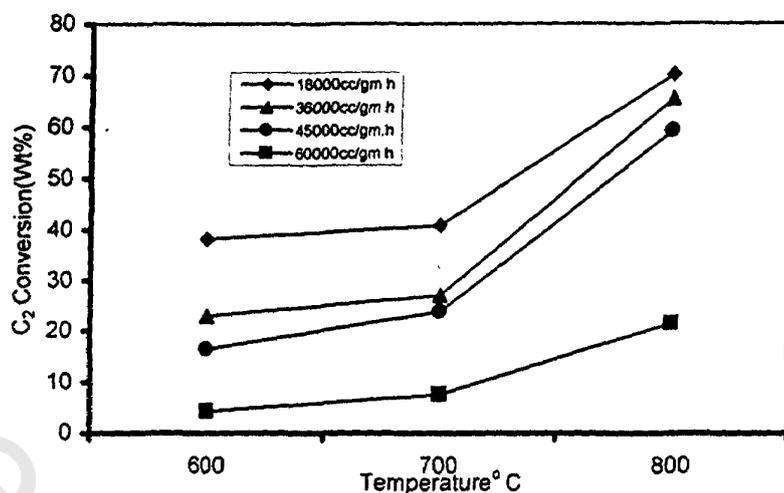


Fig (21.a) . Conversion versus temperatures of C₂ - alkane on Ir / γ -Al₂O₃ catalyst at different space velocities .

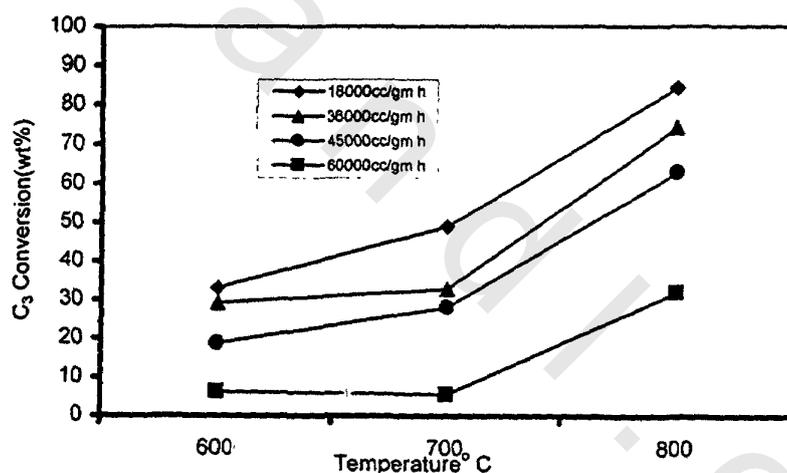


Fig (22.a) . Conversion versus temperatures of C₃ - alkanes on Ir / γ -Al₂O₃ catalyst at different space velocities .

At constant temperature the conversion decreased in the sequence of increasing of space velocity .i.e. conversion at 18000 > 36000 > 45000 > 60000cc.gm⁻¹h⁻¹ or in the order of contact time decrease as shown in Fig. (4.21.b,4.22.b.) , and Table (4.17) .

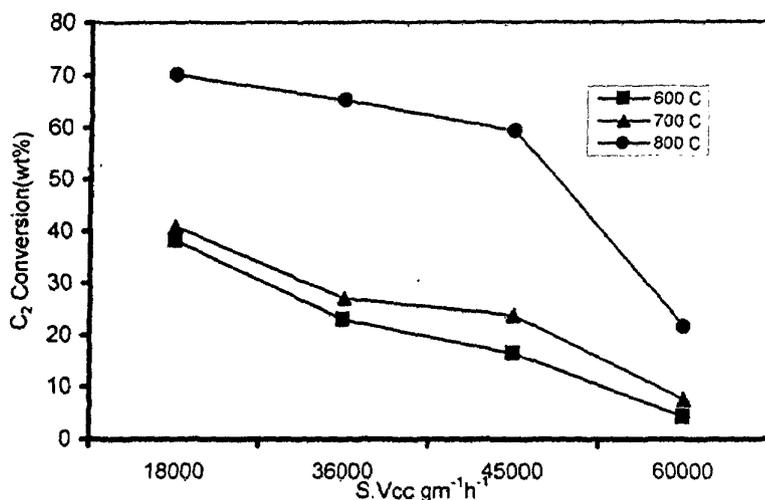


Fig (4.21.b) . Conversion versus space velocities of C₂ – alkane on Ir catalyst different temperatures .

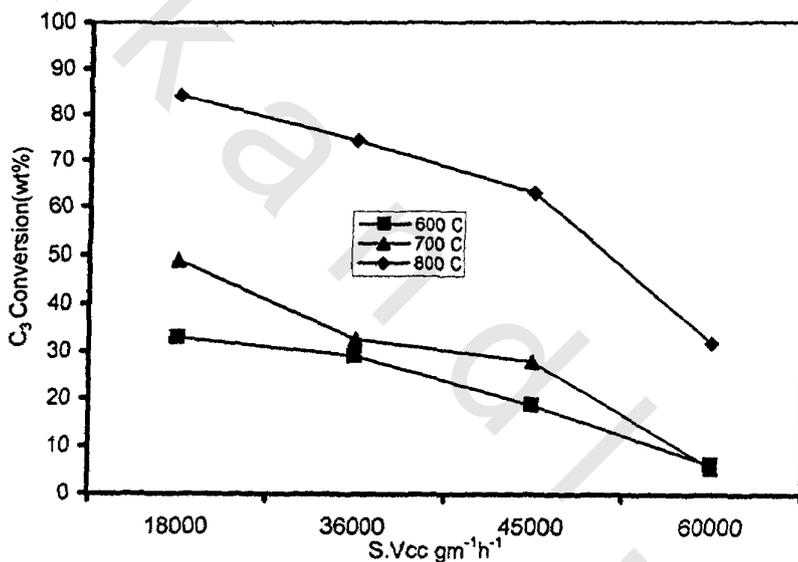


Fig (4.22.b) . Conversion versus space velocities of C₃ – alkanes on Ir / γ-Al₂O₃ catalyst at different temperatures .

Generally , the space velocity 18000cc.gm⁻¹h⁻¹ and the temperature 800°C are the optimum condition for obtaining the highest conversion percentage of ethane and propane .

Table (4.17) . Conversion of C₂- and C₃- alkane on Ir / γ-Al₂O₃ catalyst a

the studied conditions .

Temperature	600 °C		700°C		800°C	
Space Velocity ccg ⁻¹ .h ⁻¹	C ₂	C ₃	C ₂	C ₃	C ₂	C ₃
18000	38.22	32.98	48.97	48.97	70.12	84.25
36000	22.9	29.11	27.02	32.72	65.21	74.32
45000	16.38	18.74	23.73	27.94	59.23	62.94
60000	4.27	6.21	7.52	5.61	21.44	31.83

4. 3. 3. 2. 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 differed according to 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⁻¹h⁻¹ exhibited the most efficient velocity for complete conversion of both butanes and pentanes because this velocity offered the suitable enough time for complete reaction .

The temperature 800°C is the preferred one at all the studied space velocities used because the CO₂- reforming of N.G. is highly endothermic reaction , as shown in

Fig(4.23.A-C , 4.24.A-C) .

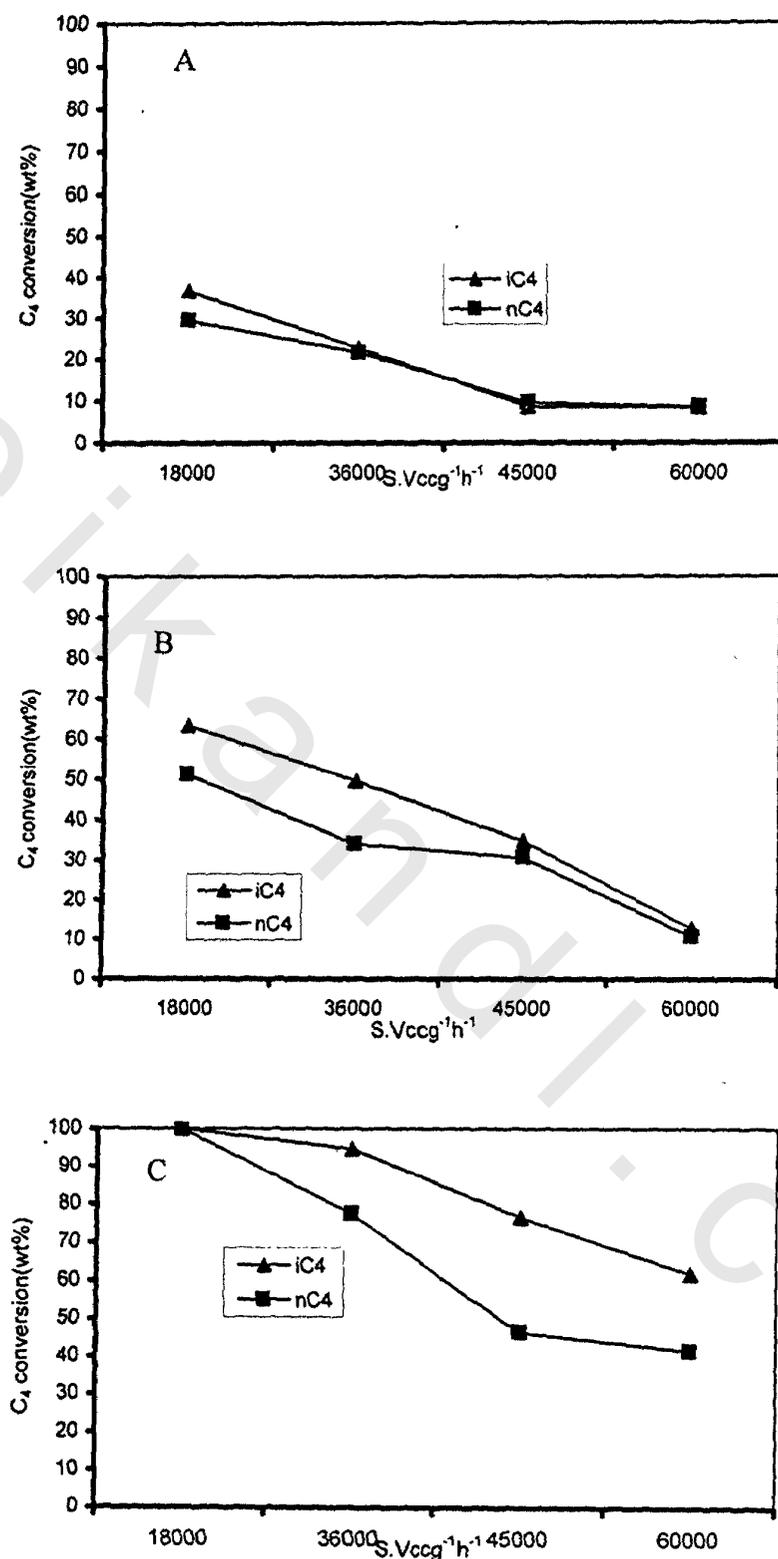
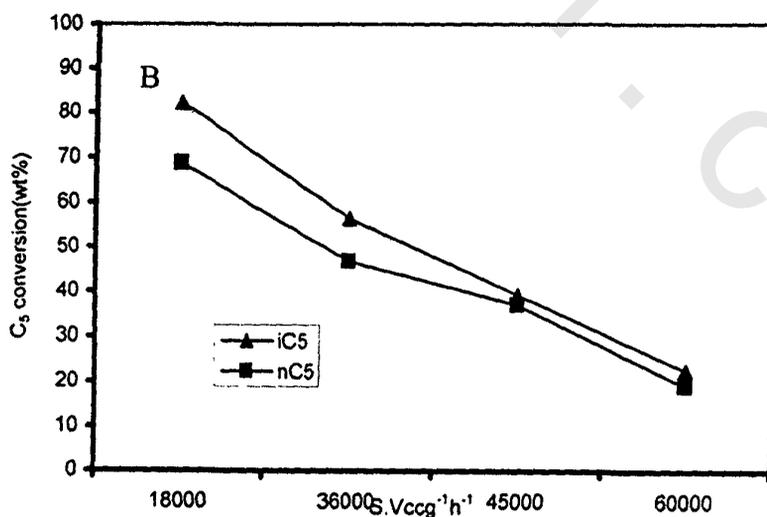
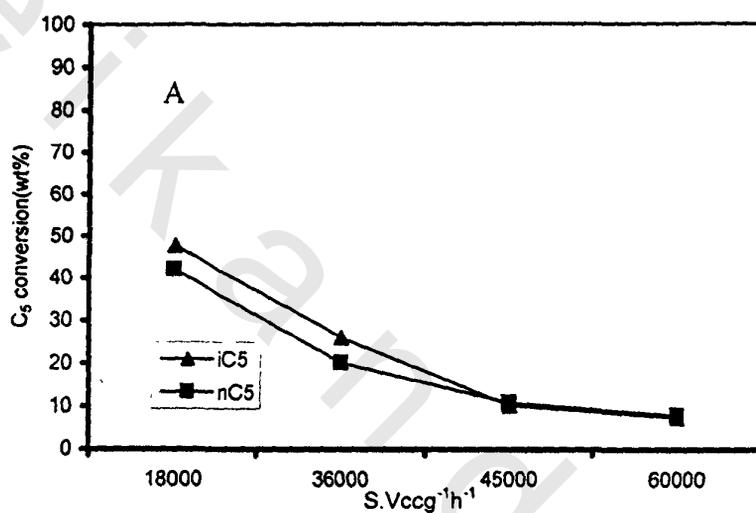


Fig (4.23A-C) . Conversion versus space velocities of C₄ – alkanes on Ir / γ - Al₂O₃ catalyst at temperatures A (600) , B (700) , C (800) °C .

At constant temperature , it is clear that the butanes (normal and iso-) and pentanes(normal and iso-) conversion decreased in the sequence of increasing of space velocity .i.e. conversion at 18000 > 36000 > 45000 > 60000 ccg⁻¹h⁻¹ i.e. in the order of decreasing contact time, as shown in Fig. (4.23.A-C , 4.24.A-C) and Table (4.18 , 4.19).



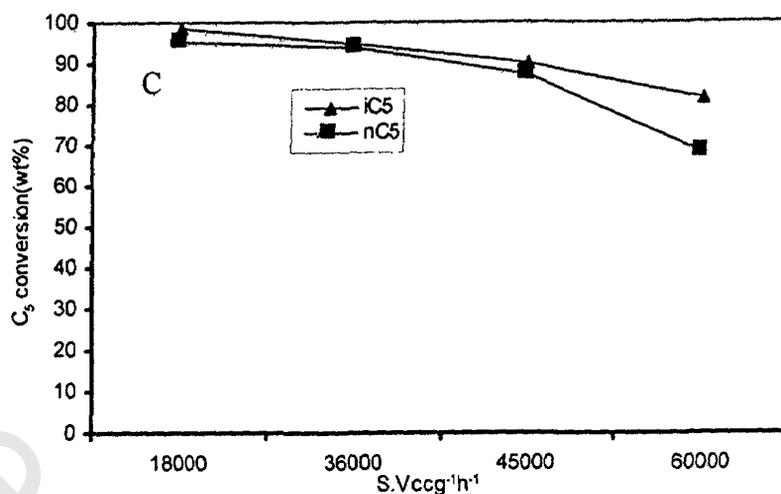


Fig (4.24. A-C) . Conversion versus space velocities of C₅ – alkanes on Ir / γ - Al₂O₃ catalyst at temperatures A (600) , B(700) , C (800) °C .

There is approximately a complete conversion at space velocity 18000 ccgm⁻¹h⁻¹ and 800°C for butanes compound , the data given in Table (4.18)

Table (4.18) . Conversion of i-C₄- and n-C₄-alkanes on Ir / γ - Al₂O catalyst at the studied conditions .

Temperature	600 °C		700°C		800°C	
	<i>i</i> -C ₄	<i>n</i> -C ₄	<i>i</i> -C ₄	<i>n</i> -C ₄	<i>i</i> -C ₄	<i>n</i> -C ₄
Space Velocity ccg ⁻¹ .h ⁻¹						
18000	36.7	29.46	63.36	51.8	100	100
36000	22.64	21.61	49.56	34.04	94.62	77.4
45000	8.56	9.49	34.75	30.62	76.47	46.46
60000	8.37	8.46	12.73	10.66	61.88	41.58

Also, the four different space velocity the conversion of iso-butaness and iso-pentaness was generally higher than n- butaness and n- pentaness conversion at the three different temperatures, this may be occurs because the iso-components is more active due to the branching in the chain , Table (4.14 , 4.15) .

Table (4.19) . Conversion for *i*-C₅- and *n*-C₅- alkanes on Ir / γ - Al₂O₃ catalyst at the studied conditions .

Temperature	600 °C		700°C		800°C	
	<i>i</i> -C ₅	<i>n</i> -C ₅	<i>i</i> -C ₅	<i>n</i> -C ₅	<i>i</i> -C ₅	<i>n</i> -C ₅
Space Velocity ccg ⁻¹ .h ⁻¹						
18000	47.74	41.96	82.14	68.73	98.77	95.34
36000	26.03	20.1	56.51	46.79	94.76	93.6
45000	10.21	10.8	39.27	37.02	90.07	86.98
60000	7.45	7.91	22.6	19.14	81.62	68.06

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

4. 3. 3.3. Hexanes and heptanes conversion :-

The conversion of hexanes and heptanes increased with increasing the temperature , 800°C is the most efficient degree giving high conversion percentage as shown in Fig (4.25.a , 4.26.a) because the CO₂ - reforming of N.G. is highly endothermic reaction .

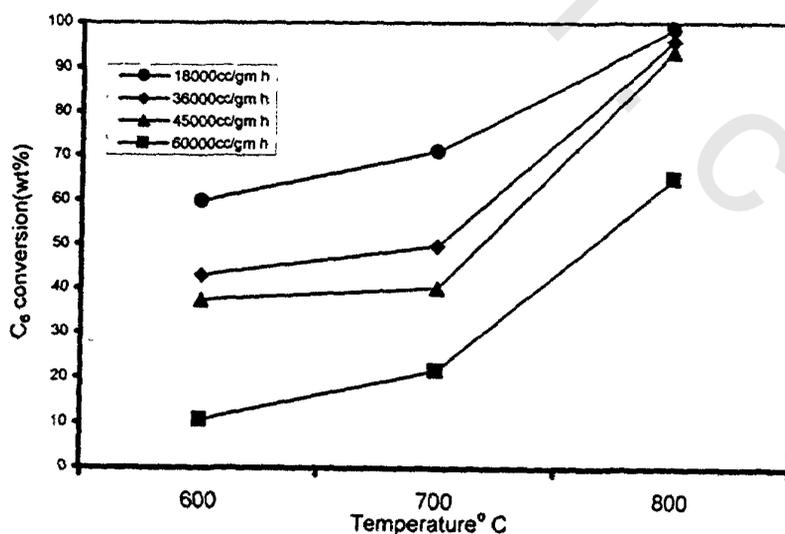


Fig (4.25.a) . Conversion versus temperatures of C₆- alkanes on Ir / γ - Al₂O₃ catalyst at different space velocities .

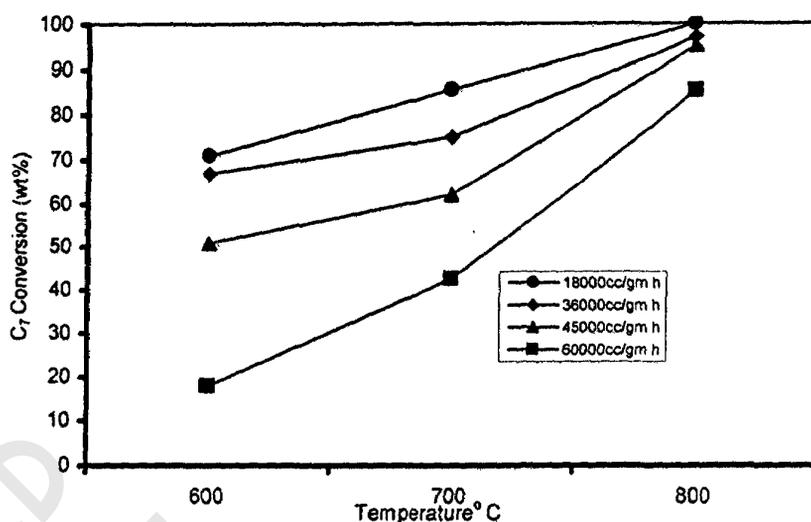


Fig (4.26.a) . Conversion versus temperatures of C_7 - alkanes on Ir / γ - Al_2O_3 catalyst at different space velocities .

At constant temperature the conversion decreased in the sequence of increasing of space velocity .i.e. conversion at 18000 > 36000 > 45000 > 60000 $ccg^{-1}h^{-1}$ i.e. in the order of decreased contact time .

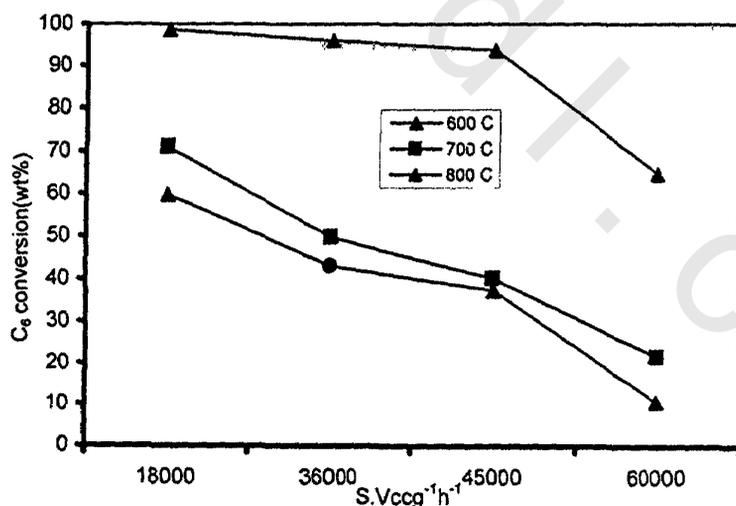
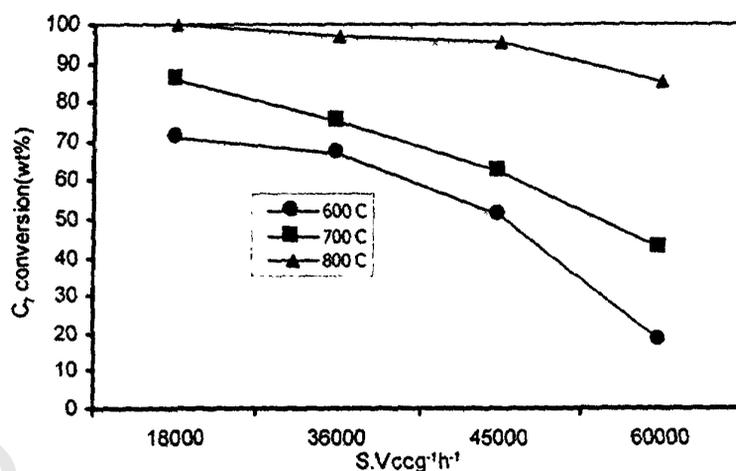


Fig (4.25.b) . Conversion versus space velocities of C_6 - alkanes a on Ir/ γ - Al_2O_3 catalyst at different temperatures .



Fig(4.26.b) . Conversion versus space velocities of C₇- alkanes on Ir / γ- Al₂O₃ catalyst different temperatures .

The highest conversion occurred at the space velocity 18000 ccg⁻¹h⁻¹ for all the three studied temperatures as shown in Fig (4.25.a , 4.26.a) due to the highest contact time which is suitable enough for complete reaction.

There is approximately a complete conversion at space velocity 18000cc.gm⁻¹h⁻¹ and 800°C for hexanes and heptanes compound Table (4.20)and shown in Fig(4.25.b , 4.26.b) .

Table (4.20) . Conversion of C₆⁺- and C₇⁺- alkanes on Ir / γ-Al₂O₃ catalyst at the studied conditions .

Temperature Space Velocity ccg ⁻¹ .h ⁻¹	600 °C		700°C		800°C	
	C ₆ ⁺	C ₇ ⁺	C ₆ ⁺	C ₇ ⁺	C ₆ ⁺	C ₇ ⁺
18000	59.77	70.91	71.06	85.59	98.69	100
36000	43.06	66.89	49.78	75.1	96.01	97.01
45000	37.43	50.8	40.22	62.19	93.67	95.26
60000	10.68	17.86	21.62	42.52	64.81	85.26

4. 3. 4. Formation of syngas (H₂ and CO) :-

The H₂ and CO selectivity using Ir / γ-Al₂O₃ catalyst at different conditions were given in Table (4.21) .

It has been found that the selectivity of both H₂ and CO increased as a function of temperature for all the studied velocities . Also ; at constant temperature the selectivity of both H₂ and CO decreased with increasing the space velocity .

Table (4.21) . H₂ , CO selectivity on Ir / γ -Al₂O₃ catalyst at different temperatures and space velocities .

Temperature Space Velocity ccg ⁻¹ .h ⁻¹	600°C		700°C		800°C	
	H ₂ %	CO%	H ₂ %	CO%	H ₂ %	CO%
18000	0	13.78	2.01	7.76	4.35	22.05
36000	0	0	2	3.52	3.08	12.93
45000	0	0	0	1.92	1.73	8.11
60000	0	0	0	0	0.14	6.88

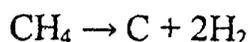
Ir / γ -Al₂O₃ catalysts showed moderate selectivity to H₂ and CO at 18000 , 36000 cc.g⁻¹.h⁻¹ for space velocities examined , at high reaction temperature 700 , 800°C only Table (4.21) .

Generally ; CO was detected at most of the operating conditions which was not the case with H₂ ; however ; H₂ / CO < 1 was always observed Table (4.22) Wang et al (2000) this aspect can be explained considering that CO is also involved as a product in other chemical reactions with respect to H₂(Portugal et al ; 2000) , (Bhat et al ; 1997) and (Mark et al ; 1996) .

The hydrogen can be supplied by the dry reforming reaction (DR) :-



Or by methane cracking :-



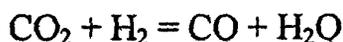
But CO can be supplied by the dry reforming reaction (DR) :-



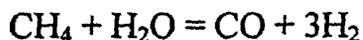
OR Boudouard reaction :-



OR (RWGS) reaction :-



OR steam reforming reaction :-



Generally, the space velocity $18000 \text{ ccg}^{-1}\text{h}^{-1}$ and the temperature 800°C are the optimum condition for obtaining the highest selectivity for H_2 and CO individually .

On the other hand ; the highest of H_2 / CO (0.57) ratio , for $\text{Ir} / \gamma\text{-Al}_2\text{O}_3$ catalysts occurred at $36000 \text{ ccg}^{-1}\text{h}^{-1}$ space velocity and 700°C temperature as shown in Fig. (27.a , b) and Table(4.22) .

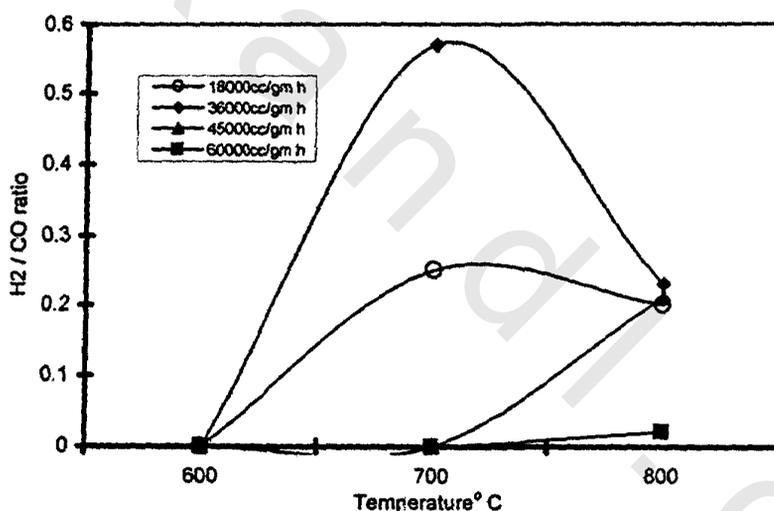


Fig .(4.27.a) . H_2 / CO ratio versus temperatures on $\text{Ir} / \gamma\text{-Al}_2\text{O}_3$ catalyst at different space velocities .

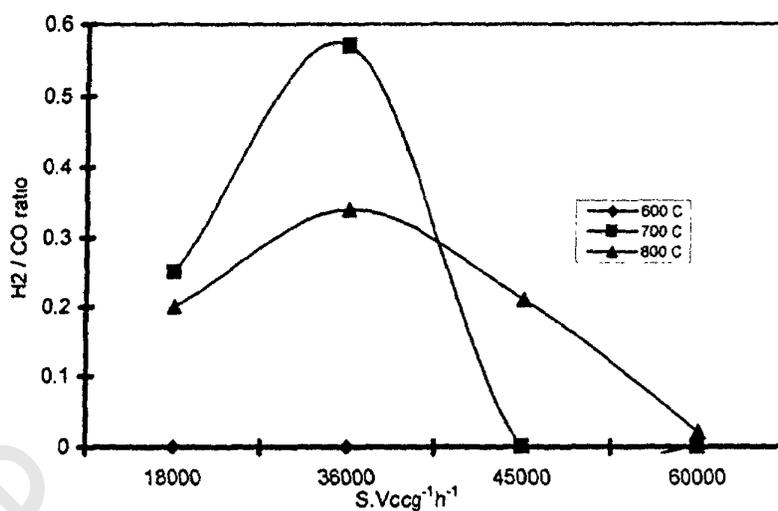


Fig (4.27.b) . H_2 / CO ratio versus space velocities on Ir / γ - Al_2O_3 catalyst at different temperatures .

Table (4.22). H_2 / CO ratio on Ir / γ - Al_2O_3 catalyst at different temperatures and space velocities .

Temperature	600°C	700°C	800°C
Space Velocity ccg ⁻¹ h ⁻¹	H ₂ /CO		
18000	0	0.25	0.20
36000	0	0.57	0.34
45000	0	0	0.21
60000	0	0	0.021