## The Use of Gas-to-Liquid Technology (GTL) to Produce Gasoline and Diesel Fuels

Dr.Khalid A. Sukkar

Petrol Technical Department, University of Technology/ Baghdad

Dr. Farah T. Jassm

Chemaical Engineering Department, University of Technology/Baghdad

Dr.Aswar A. Alwasiti

Asaw20042003@yahoo.com

Petrol Technical Department, University of Technology/Baghdad

Muayad M. Hasan

Chemaical Engineering Department, University of Technology/Baghdad

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#### **ABSTRACT**

The conversion of methane gas to synthesis gas (CO and H<sub>2</sub>) and then into clean liquid fuels via Fischer–Tropsch synthesis is investigated in the present work. The effects of the catalyst type, pretreatment conditions, and process temperature on the catalysts activity and selectivity are investigated.

The syngas production and Fischer–Tropsch synthesis were carried out in two catalytic units connected in series. The first one contains a fixed bed reactor of 128 cm<sup>3</sup>, while the second fixed bed reactor is of 68 cm<sup>3</sup>. The results of syngas production over the prepared (Pt/HY) catalyst showed excellent resistance to carbon deposition and stable performance during 20 h-on-stream at 700°C.

The Fischer–Tropsch synthesis was carried out under different temperatures of 220, 230, 240, 250, 260, and 270°C and constant atmospheric pressure. The results showed that the catalytic synthesis leads to a wide variety of products such as gasoline, diesel and waxes. It was concluded that the best operating temperature for all Fischer-Tropsch synthesis is 240°C, where, this temperature gives the highest hydrocarbons production for diesel and gasoline.

The results indicate that the  $\text{Cu-Co/Al}_2\text{O}_3$  was the most active and selective catalyst in the Fischer-Tropsch process which gives the excellent production of the desired products.

In addition, this process shows a great potential for economical production of GTL fuels in Iraq at low costs.

**Keywords:** GTL technology; Fischer-Tropsch synthesis; catalysts preparation; Gasoline and diesel.

# استخدام تكنولوجيا تحويل الغاز الى سائل لانتاج الكاوزولين وقود الديزل

#### لخلاصة

تم في هذا العمل دراسة تحويل غاز الميثان الى الغازات الخلاقة ( الهيدروجين و اول اوكسيد الكاربون) وبعدهاالى وقود سائل نظيف خلال عملية الفشرتروبش حيث تم دراسة تأثير نوع العامل المساعد وظروف المعالجات الاولية ودرجة الحرارة على فعالية العامل المساعد ونوعيته.

انتاج الغازات الخلاقة وعملية الفشرتروبش تم اجراءها في وحدتين تحويان على عامل مساعد مرتبطتين على التوالي . الاولى تحوي على مفاعل ذو الحشوة الثابتة ذو حجم ١٢٨سم٣ والاخر ذو حجم ١٨٠سم٣ . ان الغازات )المحضر اضهرت مقاومة عالية لتفكك الكاربون وسلوك ثابت خلال ٢٠ ساعة تحت درجة حرارة (Pt/Hyالناتجة ٧٠٠ درجة مئوية.

عملية الفشرتروبش تم اجرائها تحت درجات حرارية مختلفة ٢٢٠و ٢٣٠ و ٢٥٠ و ٢٦٠ و ٢٦٠ و ٢٦٠ و ٢٦٠ و ٢٦٠ و ٢٦٠ و ٢٢٠ و ٢٢٠ و ٢٢٠ و ٢٠٠ درجة حرارية وضغط جوي ثابت. اضهرت النتائج ان العامل المساعد المستخدم اعطى انواع متعددة من النواتج مثل الكازولين والديزل والشمع. وكانت افضل درجة حرارية للتشغيل هي ٢٤٠ درجة مئوية والتي اعطت اعلى انتاجية من الديزل والكازولين.

هو اكثر العوامل المساعدة فعالية في عملية الفشرتروبس  ${\rm Cu-Co/Al_2O_3}$  اشارت النتائج ان العامل المساعد والذي اعطى انتاجية رائعة من النواتج المرغوبة.

اضافة الى ذلك العملية المستخدمة اعطت مخزون عالي للاقتصاد بانتاج وقود (الغاز الى سائل) في العراق بكلفة قليلة.

## INTRODUCTION

In recent years, many changes have been introduced in petroleum industry through developing of a new process to produce clean fuels. These changes lead to improvement in the engine fuel economy and power output, reductions in the combustion noise and, more recently, in pollutant emissions of CO<sub>2</sub>, CO, NOx and particulate matter. The interest in improving the environmental protection and to promote the efficiency of the automotive motors encourages the formulation of new catalysts or development of new processes for gasoline and diesel production. Gas-to-Liquid (GTL) is one of the most effective and economic technology used to produce of liquid hydrocarbons from natural gas [1, 2, 3].

In general, the GTL technology consists of three main processes: synthesis gas (syngas) manufacturing, Fischer-Tropsch synthesis and product upgrading. Synthesis gas is a mixture of CO and  $H_2$ , which can be obtained from any carbon containing feedstock, such as natural gas. The main process for syngas production is catalytic partial oxidation of methane [2, 4]:

$$CH_4 + 1/2 O_2 \rightarrow CO + 2H_2$$
  $\Delta H2980 = -35.9 \text{ kJ/mol}$  .. (1)

On the other hand, the Fischer-Tropsch reaction represents the heart of GTL process, because it determines the product type and distributions. The highly exothermic Fischer-Tropsch reaction converts synthesis gas into a large range of linear hydrocarbons including gasoline, diesel and wax according to the following equation [5, 6, 7].

$$nCO + (2n+1) H_2 \leftrightarrow CnH_2n+2 + nH$$
  $\Delta HR = -168.8 \text{ kJ/mol}$  ...(2)

The most common Fischer-Tropsch catalysts are group VIII metals (Co, Ru, and Fe). Iron catalysts are commonly used, because of their low costs in comparison to other active metals. On the other hand cobalt catalysts give the highest yields and longest life-time and produce predominantly linear alkanes. Metal catalysts are usually supported on alumina, silica, and zeolite [1, 8, 9].

Many authors [3, 4, 8] pointed to the fact that, the design and operation of GTL process is very difficult, principally because the complex chemical reactions kinetics, so that numerous investigators have studied the the process experimentally and prepared a wide range of hydrocarbons by using different types of catalysts [5, 8, 9, 10]. Some have focused on Fe-based catalysts due to their interesting activity and selectivity towards hydrocarbons, while few of them have focused on modification of Co-based catalysts [2, 6].

Borg [11] showed that cobalt catalyst deactivate rather more rapidly then other types of catalysts (Fe based catalysts) on addition of significant amounts of water to the reaction feed. The effect is more pronounced with smaller cobalt particles. Chen et al. [12] reported that the addition of ZrO<sub>2</sub> decreases the adsorption intensity of CO, whereas it increases the amount of CO adsorbed on Co-based catalysts, which inhibits CH<sub>4</sub> formation and increased the selectivity for heavy hydrocarbons. Borg et al. [13] studied the Fischer-Tropsch synthesis and they found a clear, positive correlation between the Al2O3 catalyst pore diameter and the C5+ selectivity. The same trend was found for mesoporous silica supported cobalt catalysts. Kiss et al. [14] studied hydrothermal deactivation of silica-supported cobalt catalysts. They demonstrated that high partial pressure of water results in the formation of a phase containing mixed oxides of support and cobalt which is inactive for the synthesis.

Most of the studies performed in the GTL technology have focused on the modification of syngas reaction and only a rather limited number of papers have focused on studying the influence of reaction conditions and the type of catalysts on the activity and selectivity in the Fischer-Tropsch reaction [10–16]. It is important to mention here that the development of Fischer-Tropsch catalysts will improve the production and selectivity of the process toward the desired hydrocarbons. On the other hand GTL technology has not been applied in Iraq yet, and it is known that Iraq has large quantities of natural gas reserves. Therefore, the main objectives of the present work are:

- 1-Prepare and modify more active, selective and stable catalysts for Fischer-Tropsch reactions.
- 2-Study the effect of the main process variables on the catalyst activity and selectivity through a wide range of operation conditions.

#### **EXPERIMENTAL**

#### - Feedstock

Iraqi methane gas (98.4% purity) delivered by Al-Basra Refinery (South Refining Company) was used as a feedstock in the present investigation. Hydrogen gas (99.99%), Oxygen gas (99.8%) and Nitrogen gas (98.9%) were supplied from Al-Mansour plant (Baghdad).

#### - Chemicals

Potassium Nitrate (KNO<sub>3</sub>, 99.97%), Cobalt Nitrate [Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O], Cupper Nitrate Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, NaY-zeolite with (Si/Al) ratio of 2.6 and with extrudate shape of average size of 2x3mm, Alumina Al<sub>2</sub>O<sub>3</sub> with spherical shape and average size of 3mm (FLUKA AG company), Hexachloroplatonic Acid H2PtCl6 (40% wt Pt, Riedel De Haen AG), and Ammonium Chloride NH4Cl (BDH) are used in this work.

#### - Preparation of Pt/HY Catalyst

Pt/HY zeolite was prepared in order to be used as catalyst in syngas reactor. The Na+ ions in NaY zeolite were exchanged for NH<sub>4</sub><sup>+</sup> ions to obtain the HY form by ion exchanging the original NaY zeolite with (3 N ) ammonium chloride solution [12, 13]. The exchanged zeolite HY (86% Na+ exchange) was loaded with Pt at concentrations of 0.5 wt % by impregnation process with aqueous solution of hexachloroplatonic acid  $H_2PtC_{16}$ . The prepared solution was added dropwise to the zeolite with mixing for 4 hours at 25 °C. The mixture was then left at room temperature for 24 hours, it was stirred intermediately during this time. The mixture was then slowly evaporated to dryness over a period of 8 hours at temperature of 75°C. The resulting catalysts were dried in air at 110°C for 10 hours, then, the samples were calcined in air at 550°C for 6 hours (increasing to that temperature at a rate of 0.5°C/min ) and finally reduced to 400°C in flowing  $H_2$  for 4 hours. Then, the sample are referred to as Pt/HY catalyst and used in syngas reactor.

## - Preparation of Fischer-Tropsch Catalysts

For the operation of the second catalytic unit of Fischer- Tropsch reactions, three types of catalysts were prepared: monometallic 15%Co/Al<sub>2</sub>O<sub>3</sub>, and promoted 0.02%K-15%Co/Al<sub>2</sub>O<sub>3</sub>, and 0.05%Cu-15%Co/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by incipient-wetness impregnation method.

## Co/Al2O3 Catalyst

The Co/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by incipient-wetness impregnation [2, 14]. The support Al<sub>2</sub>O<sub>3</sub> was first calcined at  $600C^{\circ}$ for 6 h. Cobalt nitrate [Co (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O] was dissolved in deionized water and impregnated into the support using two-steps incipient wetness to produce a final catalyst with 15 wt% cobalt. Thus, 10 g of [Co (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O] was dissolved in 47 ml of distilled water. Then the solution was added to 20 gm of the alumina sample as dropwise. Impregnation was carried out at  $25C^{\circ}$  for 3 h under constant stirring. After each impregnation, the catalyst was dried in an oven at  $110C^{\circ}$ , for 24 h. After the last impregnation and drying, the catalyst was calcined in flowing dry air, at  $400C^{\circ}$ , for 5 h, using a heating rate of  $5C^{\circ}$ / min.

#### POTASSIUM PROMOTED CATALYST

The promoted  $K\text{-}Co/Al_2O_3$  catalyst was prepared by incipient-wetness impregnation method. Thus, 10 g of  $[Co(NO_3)_2.6H_2O]$  and 3 g of  $KNO_3$  were dissolved in 47 ml of distilled water. Then the solution was added to 20 gm of the alumina sample as drop wise. Impregnation was carried out at  $25C^\circ$  for 3 h under

constant stirring. Impregnated catalyst was dried in an oven at  $110C^\circ$ , for 24 h. The dried catalyst was calcined in flowing dry air, at 400  $C^\circ$ , for 5 h, using a heating rate of 5  $C^\circ$  /min. Then, the potassium promoted catalyst was called as 0.02% K - 15%Co/Al<sub>2</sub>O<sub>3</sub> catalyst.

#### COPPER PROMOTED CATALYST

The promoted Cu-Co/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by dissolving a 10 g of  $[Co(NO_3)_2.6H_2O]$  and and 10 g of  $Cu(NO_3)_2.3H_2O$  in 60 ml of distilled water. Then the solution was added to 20 gm of the alumina sample as dropwise. Impregnation was carried out at  $25C^\circ$  for 3 h under constant stirring. Impregnated catalysts were dried in an oven at  $110C^\circ$ , for 24 h. The dried catalysts were calcined in flowing dry air, at 400  $C^\circ$ , for 5 h, using a heating rate of 5  $C^\circ$  min-1. At this stage the copper promoted catalyst was called as 0.05% Cu -15%Co/Al<sub>2</sub>O<sub>3</sub> catalyst.

#### FISCHER-TROPSCH REACTIONS TEST

Fischer–Tropsch reaction was performed in the second catalytic unit. The fixed bed reactor dimensions were 20 mm ID, 30 mm OD and 210 mm height with reactor volume of 66 cm<sup>3</sup>. The reactor was heated uniformly using an electrical furnace. The temperature inside the catalyst bed was controlled through using of a thermocouple sensor type K. The reactor was fitted with accurate means for control of pressure, and gas and liquid flow rates. The experiments were conducted at atmospheric pressure. The syngas feed (CO/H<sub>2</sub>) was kept at constant ratio of 2 using hydrogen gas cylinder connected to the system. The temperature of syngas feed was controlled by using refrigeration system.

For each experiment 20 gm of catalyst was charged into the reactor. Before each run, the catalyst was dried at 110  $^{\circ}$ C in nitrogen flow for one hour and then reduced at 300  $^{\circ}$ C in hydrogen flow for three hours. The reaction conditions were as follows: space velocity (GHSV) of 1800 ml g-1 h-1, atmospheric pressure and reaction temperature was varied between 220and 270  $^{\circ}$ C.

The effluent from the reactor contains un-reacted CO and hydrogen, as well as low and high molecular weight hydrocarbons. The G.C. analysis was used to obtain product distribution. The peak areas for the reactants and products were normalized by an external standard. All of the collected data were obtained after at least 1 h on stream of reaction to ensure steady-state conditions. The basis for the selectivity calculation was the number of moles of carbon present in a given product and the total number of moles of CO converted. Then, the calculations included the selectivity of  $CH_4$ , gasoline cut ( $C_4$ – $C_{12}$ ), diesel cut ( $C_{13}$ – $C_{21}$ ), and others of high molecular weight like waxes( $C_{22}$ <sup>+</sup>), and CO conversion.

## - Catalysts Characterization

X-Ray diffraction analysis was carried out using Phillips X" Pert Pro PW 3719 X-ray diffractometer with Cu K $\alpha$ 1 and Cu K $\alpha$ 2 radiation source ( $\lambda$ =1.54056 Å and 1.54439 Å) respectively. Slits width 1/8 and 1/4 have been applied. (Tension=40 kV, Current=30 mA). The range of angles scanned was (20 to 70) on 2 $\theta$ .

On the other hand, the catalysts surface areas and pore volume were determined using (BET) method, the apparatus used was Micromeritics ASAP 2400 located in Petroleum Research Center / Ministry of Oil (Baghdad).

#### -Process Description

Figure (1) shows a view of the synthesis and Fischar Tropsch unit while figure (2) shows a schematic diagram of the GTL process and all parts of them are labeled in this figure. The GTL process apparatus consists of two catalytic units connected in series. This system was constructed at the Chemical Engineering Department/University of Technology. The first unit was specified for syngas production and the second one for the Fischar –Tropsch reactions.

In industry and academic research many process are applied to produce syngas (CO and  $H_2$ ). The main two processes are steam reforming of methane, and partial oxidation of methane [5, 13]. In the present work partial oxidation of methane is used to be the source of CO and  $H_2$  generation. Then, CO and  $H_2$  are used in the second process reactor of Fischer-Tropsch.

Syngas unit consists of a vertical tubular stainless steel reactor of 20 mm internal diameter, 30 mm external diameter and 680 mm height (reactor volume 214 cm³). The reactor is heated uniformly using an electrical furnace. The temperature at the reactor center of the catalyst bed is controlled by a thermocouple sensor type K (iron-constantan). The reactor is fitted with accurate means for control of pressure, gas and liquid flow rates. The experiments were conducted at atmospheric pressure. Flows of methane and oxygen into the reactor were adjusted to the desired ratio of methane to oxygen [3, 12]. Gases mixture was preheated to reactor temperature before entering the bed.

In the first reactor a 50 gm of Pt/HY catalyst was used. Before each run, the catalyst was dried at 110 C° in nitrogen flow for one hour and then reduced at 400 C° in hydrogen flow for three hours. The operating conditions for syngas production were selected to give the highest conversion of CO depending on many factors given in the literature on Pt/HY catalyst. The temperature was selected to be  $700\text{C}^\circ$  and the operating pressure was held constant at 1 bar [7, 11]. The methane gas flow rate was 25 L/hr. Samples of syngas products were produced in the first reactor and were analyzed in a gas chromatograph (Shimadzu GC-2014) FID and TCD by using capillary column (S.G.E., length=25 mm, I.D.= 0.22 mm, film=0.2 $\mu$ m) and using N<sub>2</sub> as a carrier gas.

The fluidized bed column was constructed of (0.1 m) diameter glass column with a height of (1m). The distributor was a perforated plate made of aluminum sheet of 0.003m thickness with about 1.2% fraction free area (14). Air from a laboratory compressor was used as the fluidizing gas. Fluidizing air was regulated with two rotameters before the perforated plate distributor. Three types of sand particle diameter were used in the fluidizing bed, 205,424 and 775  $\mu$ m (using the geometric mean particle diameter, narrow cut solids) at group B of Geldart classification. The physical properties are listed in Table(1).

Two quantities (8.5 kg and 9.5kg) of sand particles were charged into the bed to give a static bed height of about (30 cm) and (40 cm) respectively.

Air was introduced from the air bottom to the column flows upward.

The bed was first fluidized and allowed to settle. Later for various flow rate of air, the height of fluidized bed and pressure drop were measured across the bed by means of a manometer. The flow rate of air was measured using a rotameter.

The unbaffled condition was also investigated, where before the baffle modules was introduced into the bed and the system was allowed to reach a steady state.

#### RESULT AND DISCUSSION

The properties of prepared catalysts (Pt/HY, Co/Al<sub>2</sub>O<sub>3</sub>, K-Co/Al<sub>2</sub>O<sub>3</sub>, and Cu-Co/Al<sub>2</sub>O<sub>3</sub>) are compared in Table (1). The BET specific surface area of K-modified catalyst decreased from 260 m²/g for original Co/Al<sub>2</sub>O<sub>3</sub> catalyst to 238 m²/g for K-Co/Al<sub>2</sub>O<sub>3</sub> catalyst. Also, the catalyst surface area decreased to 224 m²/g when it was promoted with copper Cu-Co/Al<sub>2</sub>O<sub>3</sub>. It is important to mention here that many authors [4,11, 13] pointed to the fact that the activities and selectivity of the catalysts in Fischer-Tropsch reaction depend on the available surface area of active sites and structure of the applied catalysts.

On the other hand, it is noted that, the prepared Pt/HY catalyst (of syngas production) possesses the highest value of the surface area and pore volume as compared with Fischer-Tropsch catalysts.

Figure (3) shows the X-ray diffraction pattern of the  $\text{Co/Al}_2\text{O}_3$ , K-  $\text{Co/Al}_2\text{O}_3$ , and Cu-  $\text{Co/Al}_2\text{O}_3$  catalysts. The XRD peaks show high crystalline property of all prepared catalyst types. The diffraction peaks at 45.7° and 66.6° are attributed to the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. No peaks of Cu and K or their compounds are detected, indicating that Cu and K were dispersed on the support as a monolayer or formed spinel-like or tridymite-like structure with no detectable interaction between the promoter and support.

It is important to mention here, that the pretreatment conditions of catalyst preparation play an important role in determining the final specification of catalyst. Therefore, Zsoldos et al. [16] who examined the influence of reduction time (1 to 4 h) on the degree of reduction, found that depending on the reduction time zero-valent cobalt phases of two different structures were obtained. Short reduction times lead to the formation of very small CoO particles, while long–term reduction results in the formation of large, bulk-like crystallites. Then, in the present work the reduction of  $\text{Co/Al}_2\text{O}_3$  catalyst by hydrogen may be proceeded in two steps:  $\text{Co}_3\text{O}_4$  to CoO and CoO to Co metal. The first step was completed by the shift of the oxide diffraction of  $36.9^\circ$  ( $\text{Co}_3\text{O}_4$ ) to  $36.5^\circ$  (CoO) and appearance of the  $42.5^\circ$  and  $61.6^\circ$  lines. The intensity of these lines depended on temperature of calcinations and reduction as CoO was gradually transformed to metallic cobalt. These observations are in agreement with the work of Agudamu et al. [30].

## - Syngas Production (Partial Oxidation of Methane)

The partial oxidation of methane was used in the present work to be the source of syngas CO and  $H_2$  in feed into the Fischer-Tropsch reactor. The advantages of the catalytic partial oxidation of methane over steam reforming of methane are the low exothermicity of the process and the high reaction rates, leading to high selectivity toward CO and  $H_2$  [3,7].

The performance of Pt/HY catalyst is shown in Table (2). The results indicate high methane conversion of about 92.5% over this type of catalysts. On the other hand, the catalyst selectivity toward CO and  $H_2$  were 95% and 96.4% respectively. This may be attributed to the best operating conditions of temperature and gases flow rates. On the other hand, the Pt/HY catalyst possesses a high surface area of 435 m²/g and a large pore volume of (0.63 cm³/g) as shown in Table (1). Then, the platinum metal is highly dispersed on zeolite support according to the applied preparation method which leads to more active sites in the bifunctional catalyst. It is known that the

Pt/HY catalyst has the ability to resist the deactivation and works and has long life time

#### FISCHER-TROPSCH REACTIONS

Fischer–Tropsch reactions of the  $\text{Co/Al}_2\text{O}_3$ , K-  $\text{Co/Al}_2\text{O}_3$ , and  $\text{Cu-Co/Al}_2\text{O}_3$  catalysts were investigated at different reaction temperatures ranging from 230 to 270oC. Figures (4), (5), and (6) show the effect of reaction temperature on product distribution in the Fischer-Tropsch reaction. Usually, the bulk of a typical gasoline consists of hydrocarbons with carbon atoms between 4 and 12 per molecule (commonly referred to as  $\text{C}_4\text{-C}_{12}$ ). The diesel fuel is the mixture of carbon chains that typically contain between 13 and 21 carbon atoms ( $\text{C}_{13}\text{-C}_{21}$ ), while,  $\text{C}_{23}^+$  represents wax of heavy molecular weight hydrocarbons. Therefore, the product distributions in the present investagation are represented in terms of gasoline cut, diesel fuel cut, and waxes.

From the hydrocarbons product distributions that are shown in Figures (4), (5), and (6), it is noted that the Fischer-Tropsch products contain large amounts of normal paraffins. Thus, the Fischer-Tropsch synthesis product is suitable to apply as diesel fuel, rather than for gasoline. The same conclusion was reached by Heng et al. [2], Das et al. [4], and Bartholomew et al. [10]. On the other hand, the catalyst preparation procedure, pretreatment conditions, type of promoter and reaction temperature govern the product distribution and then determine whether light or heavy hydrocarbons are produced. Then, Figures (4), (5), and (6) mainly point to the constant reaction temperature effect on the product distribution. It was concluded that the temperature of 240 °C represents the best reaction temperature for all three types of prepared catalysts (Co/Al<sub>2</sub>O<sub>3</sub>, K-Co/Al<sub>2</sub>O<sub>3</sub>, and Cu-Co/Al<sub>2</sub>O<sub>3</sub>).

Usually, Fischer-Tropsch reactions include a side reaction called the water-gas shift (WGS) reaction which is regarded as the major problem that lowers the desired fuels selectivity [9]. Then, the reaction results indicated that the activity of water-gas shift (WGS) reaction is very small with the incorporation of potassium (K) and cupper (Cu) promoters. These promoters can inhibit the hydrogenation ability, suppress the formation of methane, and enhance the selectivities to olefin and higher molecular weight products (i.e. diesel fuel). The same observation was noted by Sadaghiani [8].

The catalytic stability with time on stream is shown in Figure (7). The initial activity is stable for all catalyst types, but, the activity rapidly decreases as the reaction time becomes longer. The performance of Fischer Tropsch catalysts in this case was studied at 240oC (the best reaction temperature). It is important to mention here that the deactivation behavior of cobalt catalysts is mainly due to the following reasons: oxidation of metal cobalt, metal migration into the support lattice resulting in the formation of the inactive Fischer-Tropsch compounds (e.g. aluminate), the aggregation and growth of metal cobalt on the surface of the catalyst and the loss of metal cobalt because of attrition [14, 17]. The results show that the introduction of small amounts of K or Cu has a strong impact on the properties of Co/Al2O3 catalyst. Then, the addition of Cu as promoter was found to have a remarkable effect on the deactivation of catalyst during the Fischer–Tropsch reactions as shown in Figure (6). Therefore, the Cu-Co/ Al2O3 catalyst is regarded as the most stable catalyst which gives 68% of total CO conversion to hydrocarbon products.

On the other hand, it was observed that as the reactions proceeded the catalyst pore system was filled with waxes products that were formed during the Fischer-Tropsch reactions, thus, affecting the carbon monoxide conversion and then decreasing catalyst activity.

#### **CONCLUSIONS**

- 1- The results indicate that the Cu-Co/Al2O3 catalyst is the best catalyst in which shows the highest CO conversion of 68 % coupled with good stability.
- 2- The results indicate that the best operating temperature for all catalysts is 240oC. This temperature gives the highest hydrocarbons yield.
- 3- The application of GTL technology in Iraq is important and it is possible to be a new source for clean fuels depending on Iraq natural gas reserves.

#### **ACKNOWLEDGMENT**

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Fischer-Tropsch Catalysts Syngas Catalyst Pt/HY Co/Al2O3 **Property** K-Cu-Co/Al2O3 Co/Al2O3 Metal &Promoter 0.5 % Pt 15% Co 15% Co 15% Co Content (wt%) 0.02 % K 0.05 %Cu Surface Area 435 260 238 224 (m2/g)Pore Volume 0.63 0.41 0.35 0.31 (cm3/g)**Chlorine Content** 0.15 0.22 0.23 0.23 (wt%)

Table (1) Properties of prepared catalysts.

Table (2) the performance of Pt/HY catalyst.

Catalyst	Reaction	CH4	CO	H2	H2/CO
	Temperature	Con.%	Selectivity	Selectivity	ratio
	oC		%	%	
Pt/HY	700	92.5	95	96.4	2.0





(a) (b)
Figure (1) View of the full GTL experimental apparatus (two catalytic units in series), (a) Syngas Production Unit (b) Fischer-Tropsch Production Unit.

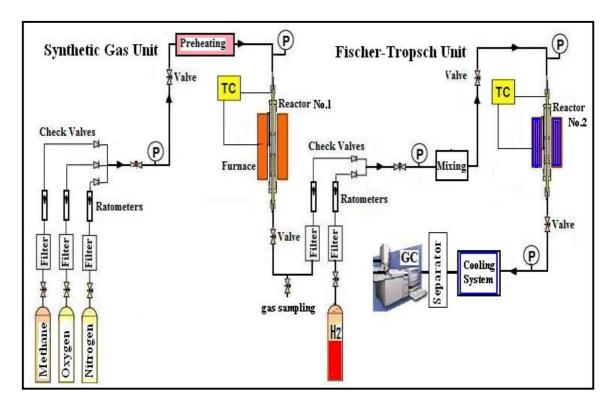


Figure (2) Schematic diagram of the full GTL experimental apparatus.

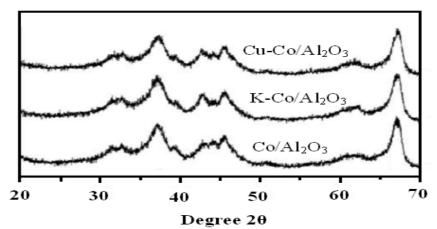


Figure (3) X-ray diffraction pattern of the prepared Fischer-Tropsch catalysts.

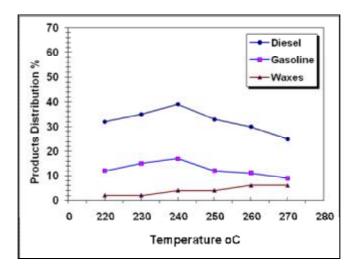


Figure (4) Effect of reaction temperature on products distribution (diesel, gasoline and waxes cuts) using  $Co/Al_2O_3$  catalyst.

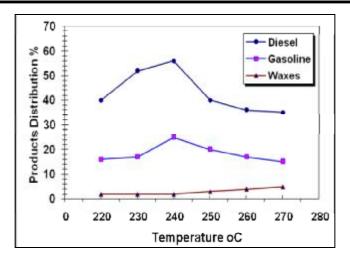


Figure (5) Effect of reaction temperature on products Distribution (diesel, gasoline and waxes cuts)
Using modified- Co/Al<sub>2</sub>O<sub>3</sub> catalyst.

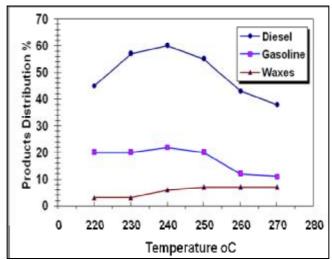


Figure (6) Effect of reaction temperature on products Distribution (diesel, gasoline and waxes cuts) using Modified Cu- Co/Al<sub>2</sub>O<sub>3</sub> catalyst.

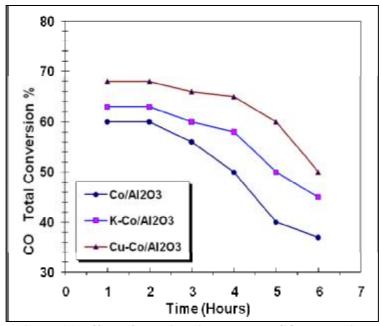


Figure (7) Effect of reaction time on total CO conversion at 240°C (catalysts stability).

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