# Conversion of ethanol to acetaldehyde using (NiO/Al<sub>2</sub>O<sub>3</sub>) as a catalyst

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# تحويل الايثانول إلى الاستلديهايد باستخدام (NiO/Al<sub>2</sub>O<sub>3</sub>) كعامل مساعد

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الخلاصه:

تم دراسة عملية تحول الايثانول الى الاسيتالديهايد في مفاعل انبوبي تكاملي بقطر 2 سم وطول 80سم والدراسة تختص بايجاد افضل الظروف من درجة حراره التفاعل ،معدل الجريان،تركيز الايثانول وتحضير افضل عامل مساعد كما يتضمن دراسة ميكانيكية التفاعل. ان طريقة الزهرجة (ازالة الهدروجين) للكحول الاثيلي لغرض انتاج مادة الاسيتالديهايد ذات فوائد عديدة مقارنه مع العمليات الانتاجيه الاخرى وتتلخص هذة الفوائد بان المادة الاوليه الخام (الايثانول) تكون رخيصة الثمن والتفاعل يتم تحت الضغط الجوي. تم تحضير العامل المساعد (الايثانولي) مختبريا وتم التفاعل بأستخدام عشرة غرامات من العامل المساعد وبدرجة حراره تتراوح من 200 – 205 درجه مئويه تحت الضغط الجوي وتركيز الايثانول كان بنسبه مئويه مولية تتراوح من (90% - 100%) وبمعدل جريان يتراوح من 1-4 (ملي لتر /دقيقه) حيث اعطى العامل المساعد (الاكراري الالالية الالالية الخام العامل المحول الأثلي في تلك النقطة بلغ 74

#### Abstract

The conversion of ethanol to acetaldehyde in an atmospheric integral up flow reactor (inside diameter and height equal to 2.0 and 80 cm respectively)which was studied in order to find the optimum reaction temperature, the effect of ethanol concentration and flow rate according to the type of catalyst used.

The proposed dehydrogenation method offers several advantages over the various production processes advantages are cheap raw (ethyl alcohol) and the reaction occur at atmospheric pressure

The (NiO/Al<sub>2</sub>O<sub>3</sub>) catalyst was prepared in laboratory using ten gram of catalyst in the reaction, the studied temperature range was  $250-325^{\circ}$  C at atmospheric pressure, the ethanol mole Concentration ranging between 90% - 100% mole and the flow rate was 1-4 ml/min

Where  $(NiO/Al_2O_3)$  catalyst was employed the maximum yield of acetaldehyde is 43% mole and the conversion of ethyl alcohol at the optimum reaction conditions is 74% mole.

# **1- Introduction**

The conversion of ethanol to acetaldehyde method offers several advantages over the various production processes these advantages are cheap raw material(ethyl alcohol) and The reaction occurs at atmospheric pressure, this method is a promising process for the production of various product such as acetaldehyde, ethyl acetate, acetic acid, ethylal, etc. [1] and acetone [2].Acetaldehyde can be produce by hydration of Acetylene; partial oxidation of ethanol or ethylene, and oxidation or dehydrogenation of ethanol [3]

The disadvantage of partial oxidation method is using an expensive catalyst and high reaction temperature [4-5] the hydration of acetylene involves the use of mercury as mercuric complex which is toxic material [5]. Thus, the alternative ethanol dehydrogenation method has been very interesting for production acetaldehyde. This method uses only one reactant, ethanol which can be abundant recourse such as fermentation of agricultural products additionally, the co-product of this reaction is hydrogen which can be used as energy source for fuel cell [6]

# 2- Materials and Equipments:

## 2.1 Gases:

High grade quality nitrogen (99.99 %) was used. Nitrogen was used in the beginning in order to ensure good temperature distribution in the reactor, to purge the air from the reactor and at the end of experiment to purge off the gases from all the system

# 2.2 Chemicals:

Ethyl alcohol with different concentrations was used. Table (1) shows the molar ratio of water to ethanol used and the subsequent concentration of ethanol.

Moles Ethanol : Moles H <sub>2</sub> O	Ethanol (%) mole
10 :0	100
9.5 : 0.5	95
9.3 : 0.7	93
9 :1	90

 Table (1) Molar <u>Ratio of Water to Ethanol and the Subsequent Ethanol</u> Concentration.

## 2.3 Catalyst:

 $NiO/Al_2O_3$  catalyst was used The specifications of this catalyst is given in Table (2)

Weight Composition	Particle Density (kg/m <sup>3</sup> )	Surface Area $(m^2/g)$	Pore Volume (m <sup>3</sup> /kg)	Form (mx10 <sup>-3</sup> )	Porosity (µm)
$\begin{split} NiO &= 10\%\\ Al_2O_3 &= 90\% \end{split}$	1011	33	1.238 x 10 <sup>-3</sup>	5x5	0.06421

Table (2) Specification of the Used Catalyst.

#### 2.4 Equipment:

The experiment apparatus is shown in schematic diagram in figures (1). The apparatus consists of the following parts:



#### 2.4.1 Ethyl Alcohol Container:

This container is made of Pyrex glass, with a volume of 3 liters used for storing the ethyl alcohol-water mixture.

#### 2.4.2 Feed Burettes:

Burette is used to observe and assess the flow rate of ethyl alcohol prior to entering the integral flow reactor.

#### 2.4.3 Needle Pump:

The needle pump is used in feeding the ethyl alcohol, it operates using variable flow rates and pulses, the maximum and minimum flow rate are 4 and 0.06 liter/h respectively.

#### **2.4.4 Integral Flow Reactor:**

The reactor is constructed of stainless steel, it has an inside diameter and length (2 and 80 cm) respectively. It consists of two sections, evaporation and preheated section and a reaction section.

The evaporation and preheating section length is about 70 cm filled with small glass particles with a diameter of 8 mm. The reaction section contains the catalyst bed and small glass particles in order to support the catalyst bed. The weight of the catalyst bed is 10 g and the LHSV ranging from 6-60  $h^{-1}$  for type of catalyst used. The flow of the feed is up flow.

#### 2.4.5 Heating Tape:

Heating tape is used to heat the reactor to the required reaction temperature, the tape length is about 1.5 m, its power is 400 W and its maximum temperature is 450 °C. This equipment was produced by Electro thermal Engineering Ltd.

#### 2.4.6 Temperature Indicator and Controller:

TIC is used to maintain constant temperature in the reactor; it consists of digital indicator and type K sensor.

## 2.4.7 Condenser:

Shell and tube heat exchanger are used consequently in order to condensate the vapors that result from the integral flow reactor. 70 % ethyl alcohol was used as a cooling fluid in the chiller.

## 2.4.8 Reservoir:

The reservoir volume is about 500 ml made of stainless steel used as a reservoir of that product and it contains outlet line to pass the gases and uncondensed vapors to the scrubber.

## 2.4.9 Scrubber:

A 350 ml Pyrex scrubber was used to scrub the uncondensed vapors; distilled water was employed in the scrubbing process.

# **3- Experimental Work:**

## 3.1 catalyst preparation

NiO based catalysts were prepared by impregnation using  $Al_2O_3$  as supporting material. Ni  $(NO_3)_2$  was used as a Ni(OH)<sub>2</sub> precursor (reaction 1).And Al(NO<sub>3</sub>)<sub>3</sub>., was used as a Al(OH)<sub>3</sub> precursor (reaction 2).

Ni 
$$(NO_3)_2 + 2 \text{ NaOH} \longrightarrow Ni(OH)_2 + 2 \text{ NaNO}_3$$
 (reaction 1)

 $(reaction 2) \operatorname{Al}(\operatorname{NO}_3)_3 + 3\operatorname{NaOH} \rightarrow \operatorname{Al}(\operatorname{OH})_3 + 3\operatorname{NaNO}_3$ 

The precipitate is a white hydrogel then filtrated and washed with distilled water , kneaded and perfectly extruded to have 5 mm extruded. The extruded were dried at room temperature then at 120°C for 3 hours in an oven. Calcinations, as the final step in preparation, was performed in a muffle furnace at 500°C for 3 hours with using  $2^{\circ}$ C/min temperature rise rating.

Ni (OH)<sub>2</sub> 
$$\xrightarrow{500^{\circ}C}$$
 NiO + H<sub>2</sub>O  
2Al(OH)<sub>3</sub>  $\xrightarrow{500^{\circ}C}$  Al<sub>2</sub>O<sub>3</sub> + 3H<sub>2</sub>O

#### **3.2 Experimental Procedure:**

The dehydrogenation of ethyl alcohol was carried out in the apparatus previously described in figures (1); the test procedures are as follows:

- 1- In the beginning nitrogen is used in order to purge off the air from the system. Then the reactor is heated to the desired temperature for about half an hour.
- 2- After reaching the desired temperature, wait a quarter of an hour, with continuing passing of nitrogen in order to ensure a good temperature distribution in the reactor, then the nitrogen valve is stopped. A prespecified flow rate of ethyl alcohol is set on, vaporization of ethyl alcohol occurs in the preheating section of the reactor.
- 3- The ethyl alcohol vapor reacts over the catalyst bed at the specified temperature and flow. The vapor products passes through the shell and tube condenser operating at a temperature range of (-2 to -8 °C). The condensed liquid products namely untreated ethanol, acetaldehyde, acetone, ethyl acetate, and water are collected in a reservoir and the uncondensed vapors and gases are fed to the scrubber to dissolve traces of acetaldehyde. Carbon dioxide and hydrogen gases are vented. The liquid products, collected in the reservoir and the scrubber, are sent to the gas liquid chromatograph.

The ethanol conversion is defined as the mole percent of ethanol reacted to that introduced into the reactor and the yield as the mole percent of the ethanol converted to the product to that introduced into the reactor. The amount of ethanol converted to the product was calculated on the basis that 1 mole of acetaldehyde ethyl acetate, water are produced from 1 moles of ethanol and 1 mole of ; acetone and Carbon dioxide are produced from 2 mole of ethanol. Carbon dioxide is determined by material balance on that basis.

#### **3.3 Analysis by Chromatography:**

The separation and analysis of the liquid products into their components were carried out by gas-liquid chromatograph (GLC). A porapack Q stainless steel column with an inside diameter of 1/8 inch and length of 2 m was used. The GLC column was connected to thermal conductivity detector (TCD); the GLC optimum conditions are given in Table (3).

			(-)	<u>r</u>				
Column	Temp.	TCD	Temp.	Initial	Temp.	Injection	Temp.	Rate
(°C)		(°C)		(°C)		(°C)		(°C/min)
250		200		170		200		5

Table (3) GLC Optimum Conditions.

Hydrogen  $(H_2)$  was used as a carrier gas at flow rate of 20 ml/min.

# 4- Reaction Mechanism:

For the formation of acetaldehyde from ethanol, the following mechanism has been proposed by Takezawa *et al.* [7] who studied ethanol dehydrogenation on magnesium oxide, and by Bowker *et al.* [8] who investigated the temperature programmed decomposition (TPD) of alcohols from a polycrystalline zinc oxide surface:

$$C_{2}H_{5}OH_{(g)} \rightarrow C_{2}H_{5}O_{(a)} + H_{(a)}$$

$$C_{2}H_{5}O_{(a)} + H_{(a)} \rightarrow CH_{3}CHO_{(a)} + H_{2}$$

$$CH_{3}CHO_{(a)} \rightarrow CH_{3}CHO_{(g)}$$

According to the conditions of reaction (Temperature of the reaction, concentration of ethanol, flow rate of feed and type of catalysts used) acetaldehyde or ethanol can be converted to acetone, acetic acid, ethyl acetate and Carbon dioxide

For the reaction pathway from acetaldehyde to acetone, two important routes have been proposed. One of these routes was proposed by Kagan *et al.* [9], proceeds in the order

(Acetaldehyde  $\rightarrow$  ethyl acetate  $\rightarrow$  acetic acid  $\rightarrow$  acetone).this routes is more suitable, beside this routes and according to Nakajima et al. [10] ethanol converted to acetone in the presence of water vapor

#### 5- Result & Discussion 5.1 Effect of Reaction Temperature:

The relationships between reaction temperature versus ethyl alcohol conversion and acetaldehyde yield are shown in Figs. (2) Using 10 g of NiO/Al<sub>2</sub>O<sub>3</sub> catalyst with different concentration and different flow rate (1, 2, 3 and 4 ml/min).

These relationships show that the conversion and yield have increased with increasing of temperature; the yield of acetaldehyde ascends to its maximum value at 300 °C then begins to descend with increasing temperature while the conversion of ethanol keeps increasing. This behavior could be explained on the following bases: the catalyst deactivation (probably due to sintering and coking) suppresses the conversion of ethanol to acetaldehyde but does not suppress the steam reforming and dehydration of ethanol [11].



Fig. (2) Effect of Reaction Temperature on Ethanol Conversion and Acetaldehyde Yield for NiO/Al2O3 Catalyst (F = 3 ml/min, 95% Mole percent concentration of ethanol)

The yield of byproduct (ethyl acetate, acetone, water and carbon dioxide) versus temperature is shown in Figs. (3). the yield of  $H_2O$  (which is the result of dehydration),  $CO_2$  (the result of steam reforming) and acetone increases with reaction temperature while the ethyl acetate yields being less.



percent concentration of ethanol)

#### 5.2 Effect of Feed Flow Rate on the Reaction:

The feed flow rate was studied at different molar ratios of ethanol to water at the optimum reaction temperature (300 °C) and using constant weight of NiO/Al<sub>2</sub>O<sub>3</sub> catalyst (10 g). Figures (4-5) shows the relationships between the feed flow rate

versus ethyl alcohol conversion and acetaldehyde yield and the byproducts yield versus flow rate respectively.



The mentioned figures show that the ethyl alcohol conversion and acetaldehyde yield increased with increasing feed flow rate until flow rate 3 ml/min, then began to decrease. This decrease is attributed to the resulting decrease in contact time of the reactant [12]. While by products yield decreased as shown in fig. (5) With increasing feed flow rate for the same reason.



Fig. (5) Effect of Ethanol Feed Flow Rate on Byproduct Yield for NiO/Al<sub>2</sub>O<sub>3</sub> Catalyst (T= 300<sup>0</sup>C, 95% Mole percent concentration of ethanol)

#### 5.3 Effect of Ethyl Alcohol Concentration:

Figure (6) shows the effect of water on acetaldehyde yield and ethanol conversion with NiO/Al<sub>2</sub>O<sub>3</sub> catalyst at optimum temperature and flow rate of (300 °C and 3 ml/min respectively) using 10 g of catalyst.

In the begging ethanol conversion and acetaldehyde yield doesn't change with little amount of water but when the concentration of ethanol reached less than 95% It has been noticed that the molar ratio of ethanol to water activates ethanol conversion and acetone yield. This behavior can be explained by the fact which says that increasing water activates the dehydrogenation reaction towards dehydration reaction [12], acetone production [13] and steam reforming [14].



Figure (7) shows the effect of molar ratio on the yield of byproduct, it has been noticed that the yield of water, acetone and  $CO_2$  increases with increasing molar ratio while the ethyl acetate decreases



Fig. (7) Effect of mole percent concentration of ethanol on Byproduct Yield for NiO/Al<sub>2</sub>O<sub>3</sub> Catalyst  $(T = 300^{0} \text{ C}, \text{ F} = 3 \text{ ml/min})$ 

#### **6**-Conclusions:

- *1* The operating conditions found for 10g catalyst are: optimum reaction temperature (300 °C), optimum flow rate (3 ml/min), concentration of ethanol can be 95% for NiO/Al<sub>2</sub>O<sub>3</sub> catalyst
- 2- Increasing the reaction temperature, consequently leads to an increase in the conversion and yield to a maximum of 74 and 43 %) respectively for NiO/Al<sub>2</sub>O<sub>3</sub> catalyst
- 3- The conversion and yield increase by increasing the flow rate until rate 3 ml/min then began to decrease. This is attributed to an increase in contact time between catalyst and ethyl alcohol(when the floe rate is 1-2 ml/min.) activates the acetaldehyde conversion to acetone while the high flow rate (4 ml/min.) will not allow to complete the ethanol conversion to acetaldehyde.
- 4- Decreasing the ethyl alcohol concentration to 95% will not change the yield of acetaldehyde but more than decreasing the ethyl alcohol concentration results in a significant increase in the ethyl alcohol conversion and the yields of acetone, carbon dioxide and water

## Refrences

1- Pedro F. Castro. Maria del Carmen Viola ,jose C.Pedregosa, Manuel F. Gomes and Maria C. Abello "Oxidative dehydrogenation of ethanol over MgCro catalysts "The Journal of the Argentine Chemical Society, Vol.97 No1,242 – 249 (2009)

**2-** Nakajima T., K. Tanabe, T. Yamaguchi, and T. Matsuzaki, "*Efficient Synthesis of Acetone from Ethanol over ZnO-CaO catalyst*", J. Chem. Soc., Chem. Commun., pp 394-395, 1987.

3- J. McKetta, Encyclopedia Of Chemical Processing and Design. Marcel Dekker, Inc. New York, vol 1, p 114, 1988;

4- Faith ,W.L.,Keyes , D.B. and Clark , R.L., Industrial Chemicals , 2<sup>nd</sup> ed. Wiley New York, 1957

5 – Marshall N., Petrochemical Processes, Technical and Economic characteristics, Gulf publishing Texas, 1989

6- Arthit Neramittagapong , Wiphada Attaphaiboon , Sutasinee Neramittagapong , " Acetaldehyde Production from Ethanol Over Ni-Based Catalysts , Chiang Mai J. Sci., Vol 35 , No.1, pp 171 - 177 , 2008

**7- Takesawa N., C. Hanamaki and H. Kobayashi**, "*The Mechanism of Dehydrogenation of Ethanol on Magnesium Oxide*", J. Catal., Vol. 38, PP. 101-109 (1975).

8- Bowker M., R.W. Petts and K.C. Waugh, J. Catal., Vol. 99, pp 53, 1986.

9- Kagan M. Ya., I.A. Sobolev and Lyubarski, Chem. Ber., Vol. 68 B, p 1140 1935.

10- Nakajima T., K. Tanabe, T. Yamaguchi, T. Matsuzaki and S. Mishima, "*Conversion of Ethanol to Acetone over Zinc Oxide-Calcium Catalyst*", J. Applied Catalysis, Vol. 52, PP (237-248), 1989.

11- Nakajima T., K. Tanabe, H. Nameta, S. Mishima, and T. Matsuzaki, "A Highly Active and Highly selective Oxide Catalyst for the Conversion of Ethanol to Acetone in the Presence of Water Vapor", J. Mater Chem., Vol. 4 (6), PP. 853-858, 1994.

**12- Kassim M.A.**, "*Kinetic Study of Ethyl Alcohol Dehydrogenation Using CuO-* $ZnO/Al_2O_3$ ", M.Sc. Thesis, Chem. Eng. Dept. University of Technology, Iraq, (1998).

**13- Serrama R., P. Patnaik, P. Sidheswaran and M. Jayamani**, "*Conversion of Ethanol to Acetone over Promoted Iron Oxide Catalysis*", J. Catal., Vol.109, PP. 298-302, 1988.

14- Liorca J., J. Sales and N. Homs, "Direct Production of Hydrogen from *Ethanolic Aqeous Solution Over Oxide catalysts*", J. Chem. Soc., Chem. Commun., PP. (641-642), 2001.

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