# TWO-STEP CATALYTIC CONVERSION OF ETHANOL TO BUTADIENE IN A FIXED BED

**Adil A. Al-Hemiri and Ameel M. Rahman**
Chemical Engineering Department – College of Engineering – University of Baghdad – Iraq

## ABSTRACT

*An investigation was conducted to study the catalytic conversion of ethanol to butadiene using a fixed bed technique. 80%MgO:20%SiO2 prepared catalyst was used in this investigation. Operating conditions 200-400°C, 0.2-3.25 h-1LHSV and atmospheric pressure were studied. The effects of mole ratio of ethyl alcohol to acetaldehyde i.e 1.5:1 up to 3:1 at various temperatures and LHSV were also investigated studied.*

*At 350°C and 0.5 h-1, and ethanol to acetaldehyde mole ratio of 2.76:1 the prepared catalyst 80%MgO:20%SiO2 gave 12 mole% per pass yield and 26 mole% ultimate yield.*

## INTRODUCTION

Butadiene(1,3-butadiene),$CH_2{=}CHCH{=}CH_2$, is a major commodity product of the petrochemical industry. Butadiene is one of the important starting material for various chemical products, such as polybutadiene (CEP Report, 2003; Egloff, 1942; and Maketta and Cunningham, 1976), which is used in the manufacturing of SBR (styrene-butadiene copolymer) elastomer, in which more than 60% is used for tiers (Aston and Szasz, 1946).

A number of processes are present and employed for producing butadiene on a commercial scale: pyrolysis of hydrocarbons (Maketta and Cunningham, 1976), for example; in the steam cracking process for producing ethylene; catalytic dehydrogenation of butane and butane fractions of petroleum refinery gases (Ruebensaal, 1970); synthesis based on acetylene as a feed stock; and dehydrogenation and dehydration of ethanol (Ramsey, 1970). the economic utilization of the first and second sources presumes the necessary of a thriving petroleum industry; hence, the countries enjoying an abundant supply of natural petroleum can exploit the first two methods. In countries where ethanol may be obtained in abundance and fairly cheaply as a by-product of sugar industry, its uses as a raw material for production of butadiene may be more advantageous. Moreover this process is simple in operation and promises better economy than the other processes.

There are two commercial methods for the conversion of ethanol to butadiene: the one-step and the two step process (CEP Report, 2003; Egloff, 1942; and Maketta and Cunningham, 1976).

In the one-step process followed in Russia, dehydrogenation and dehydration are coupled in the same reactor in the presence of a suitable dehydration and dehydrogenation catalyst (Corson, et al, 1950).

$$2C_2H_5OH \rightarrow CH_2{=}CH{-}CH{=}CH_2 + 2H_2O + H_2$$

This process is evidently simpler in operation, through purity and yield of the butadiene are less.

The two-step process, followed in the United States, involves the following reactions, carried out in two separate catalytic units.

$$CH_3CH_2OH \rightarrow CH_3CHO + H_2$$
$$CH_3CH_2OH + CH_3CHO \rightarrow CH_2{=}CH{-}CH{=}CH_2 + H2O$$

Elaborate investigation have been reported by American workers, who claim that the two-step process gives higher conversion and ensure purer product (Toussaint et al, 1947).

The present study included studying the two-step process by using MgO:SiO2 as prepared catalyst. And also study the effect of MgO on SiO2. 200-400°C, 0.2-3.25 h-1 LHSV and atmospheric pressure were applied in the present study.

## EXPERMANTAL WORK

### Catalyst Preparation

MgO:SiO2 catalyst was prepared according to Kvisle, et al, 1988 and Corson, et al, 1950)

The individual Oxides MgO and SiO2 were prepared by precipitation method. Thus the preparation consisted in acidifying to pH 4.5 about 25 ml of N brand sodium silicate (9.0% sodium oxide, 29.5% silica, specific gravity 1.41, titratable alkalinity 3.94N), dissolved in 200ml water, with 17ml of concentrated hydrochloric acid (specific gravity 1.19) dissolved in 40 ml of water. The diluted acid was added to the diluted sodium silicate with agitation and the pH was subsequently adjusted to pH 4.5. Gelation took place in about 3 minutes at pH 4.5. After standing for 1h the gel was slurried by stirring with 1 liter of water for 1h and subsequently filtered. The resulting filter cake was washed with 500 ml water for 3 times until the conductivity reached $10^{-4}$ mho. The final precipitate was dried over night in oven at 100°C.

$Mg(NO_3).6H_2O$ (128 g) dissolved in water (200 ml) was treated slowly with aqueous ammonia (200 ml, 14%). After 1h the precipitate was filtered off, washed with water (300 ml) and dried over night at 90°C.

$MgO:SiO_2$ catalyst at different composition was prepared by coprecipitation of the above precursors in order to study the effect of catalyst composition. The shaping process began after a uniform paste was obtained. The paste was admitted to a stainless steel cavity of 5mm inside diameter and was compressed at a pressure of 10 bar. Avery uniform pelleted shape paste was ejected from the cavity and put in the oven at 90°C overnight. The pellets was calcined at 500°C in dry air for 4h, after a temperature rise of 0.5°C/min. at the end of this period, the pellets taken out from the furnace and cooled down in a desiccator.

80%$MgO$:20%$SiO_2$ catalyst was prepared by coprecipitation the two precursors oxides in the desired ratio before drying over night in oven at 90°C and the final pellets were then calcined at 500°C in dry air for 4h as explained above. The properties of the prepared catalysts were listed in Table (1).

Table (1) Properties of 80%$MgO$:20%$SiO_2$ Prepared Catalyst.

| Chemical Composition | wt% |
|---|---|
| MgO | 80% |
| $SiO_2$ | 20% |
| **Physical Properties** | |
| Catalyst Form | Tablets |
| Catalyst Size(mm) | 5-3 |
| Crushing Strength, minimum average( N) | 20 |
| Pore Volume, (ml/g) | 0.314 |
| Particle Density, (g/ml) | 1.207 |
| Packed Bed Density, (g/ml) | 0.883 |
| Packed Bed Void | 0.64 |
| Surface Area, ($m^2$/g) | 180 |
| Loss on Attrition, (wt%) | 4.5 |
| Apparent Porosity (%) | 33.94 |

### Dehydrogenation Unit

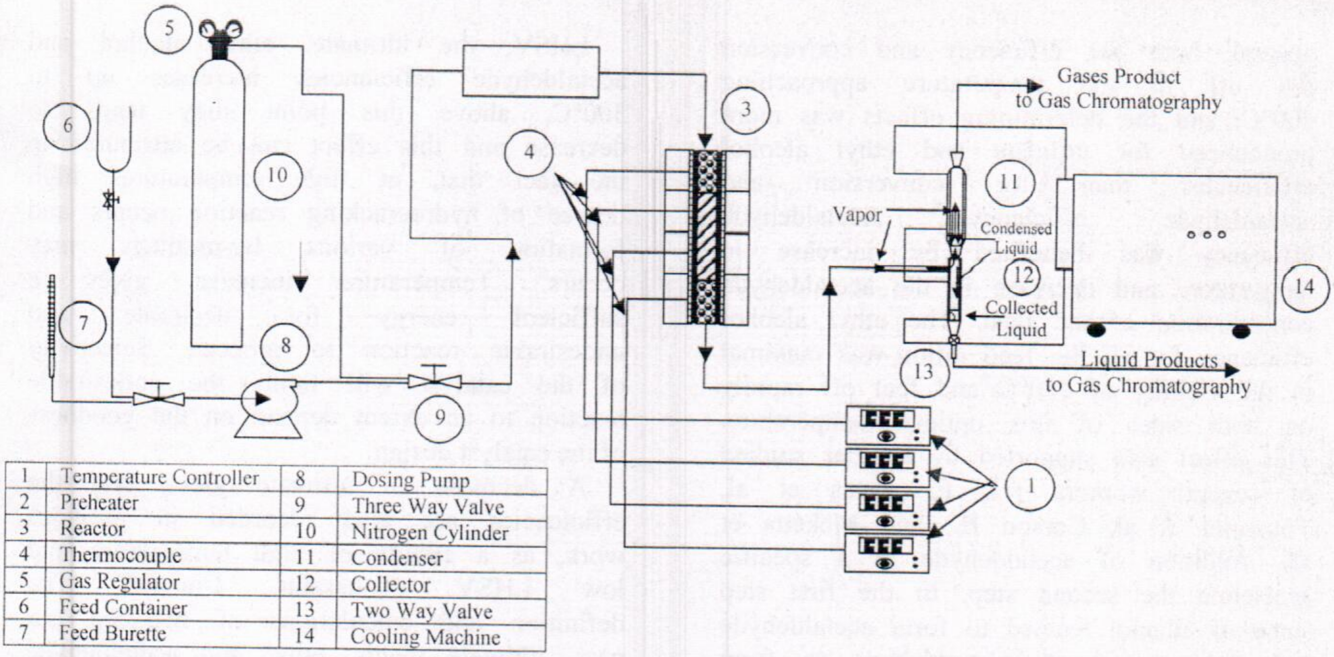
The dehydrogenation experiments were performed in a laboratory continuous plant unit. Figure (1) shows the process flow diagram.

The unit consists of feed pump, preheater, reactor, separator and cooler with appropriate control system for heating. A dosing pump is used in feeding the ethyl alcohol (and ethyl + acetaldehyde mixture).

The preheater section consists of coiled bundles of stainless steel tube (10m long with 5mm i.d). The heat was supplied by using 3KW electrical heater to heat the feed to the desired reaction temperature.

The reactor used is a carbon steel with 19 mm i.d 800 mm long and 2 mm wall thickness. The reactor was heated and controlled automatically by steel-Jacket heaters. It makes possible to measure the temperature of the catalyst bed and heaters by using chromel-alumel thermocouples. The thermocouples measured the temperature profile along the full length of the reactor.

The reactor products was cooled and collected by using pyres glass condenser and collector.



| | | | |
|---|---|---|---|
| 1 | Temperature Controller | 8 | Dosing Pump |
| 2 | Preheater | 9 | Three Way Valve |
| 3 | Reactor | 10 | Nitrogen Cylinder |
| 4 | Thermocouple | 11 | Condenser |
| 5 | Gas Regulator | 12 | Collector |
| 6 | Feed Container | 13 | Two Way Valve |
| 7 | Feed Burette | 14 | Cooling Machine |

Figure (1) Flow Diagram of Laboratory Dehydrogenation Unit

### Dehydrogenation Experiments Conditions

60 $cm^3$ of fresh catalyst was charged to the reactor between two layers of inert materials (glass balls).

The charged reactor was flushed with nitrogen 21 lit/hr for 1 h to purge off the air from the system. Then the reactor is heated to the desired temperature. After reaching the desired temperature, the nitrogen valve was closed.

A prespecified flow rate of feed was set on, vaporization and preheating of the feed occurs in the preheating section. The ethyl alcohol reacted over the catalyst at the specified feed temperature and LHSV. The product gases passed through the condenser and the final condensates were collected only after steady state operation was established and initial products were discarded.

The dehydrogenation reaction conditions employed are temperature 200 to 400°C at atmospheric pressure, liquid hourly space velocity of 0.2 to 3.25 h-1 and ethanol to acetaldehyde molar ratio of 1.5, 2, 2.5, and 3.

## RESULTS AND DISCUSSION

### *Characterization of the Prepared Catalyst*

The effect of MgO on $SiO_2$ catalyst was also studied in the this project. Figure (2) shows the effect of MgO percent on butadiene per pass and ultimate yields. The per pass yield and ultimate yield were also increased as the MgO content increases. The MgO percent are ranging from 60-80% which gives butadiene per pass and ultimate yield of 16 - 17.5 and 32.5 - 41%, respectively. This phenomena can be attributed to acid and basic sites of the contact masses, and the basicity increases with the MgO content. The specific rates of butadiene formation increase with the MgO content up to 80% , but pure MgO is inactive. This together with the fact that sepiolites which contain Si-O-Mg entities, also transform ethanol into butadiene, suggest that the catalytic activity involves factors other than the presence of acidic and basic sites.

### *Effect of Ethyl Alcohol to Acetaldehyde Feed Ratio*

The effect of ethyl alcohol to acetaldehyde mole ratio was also investigated in this study. Figures (3) represent the effect of varying the mole feed ratio at 250-400°C, 0.5 $h^{-1}$ LHSV and atmospheric pressure using 80%MgO:20%$SiO_2$ catalyst.

Evidently, the optimal feed ratio was a function of temperature. 2.76 ratio being the optimal at 400°C (41.5% ultimate yield), 3 ratio at 350°C (39.7% ultimate yield), and 3 to 1.5 ratio at 250-300°C (33.2-36.8% ultimate yield). Within the range covered by Figs. (3-6), conversion (butadiene yield) was benefited at all temperatures by increasing the acetaldehyde concentration in the feed. In general, both the efficiency and conversion fell off in the temperature approaching 400°C, and the determining effects was more pronounced for ultimate and ethyl alcohol efficiencies than for conversion and acetaldehyde efficiency. Acetaldehyde efficiency was benefited by increase in temperature and decrease in the acetaldehyde concentration of the feed. The ethyl alcohol efficiency for all the feed ratios was maximal in the vicinity of 350°C and feel off rapidly on both sides of this optimal temperature. This effect also supported by another studied of several workers (H. E. Jones et al, Toussaint et al, Corson B., and Mcketta et al). Addition of acetaldehyde in a specific accelerate the second step. In the first step some of ethanol reacted to form acetaldehyde and then react with acetaldehyde to form butadiene.

The addition of acetaldehyde not only increase the butadiene yield but also decreases the amount of ethylene, i. e., the butadiene selectivity increases. The use of mixed feed corresponds to the second stage of the two-step process wherein acetaldehyde is produced from ethanol is a first step and butadiene is formed in a separate (second) step from the mixed ethanol, acetaldehyde feedstock. The initial generation of acetaldehyde is avoided and the proposed rate limiting step is the actual transfer of hydride from the surface.

### Effect of Temperature and LHSV on the Butadiene Yield and Selectivities

In this section the effects of feed rate and temperature are studied over the two commercial and prepared catalysts. The effect of LHSV is explained in Figs. (7-10). The overall and ethanol efficiencies were maximal at 0.43-0.6 $h^{-1}$ over the studied catalysts. Butadiene per pass yield decreases approximately linearly as the feed rate was raised from 0.2 to 1.75 $h^{-1}$ over the temperature range of 250-400°C as shown in Figs(7).

The effect of LHSV and temperature on the ultimate yield, ethyl alcohol and acetaldehyde efficiencies are illustrated in Fig.(8-10) for the two commercial and prepared catalysts as the reaction temperature increases with decreasing LHSV, the ultimate, ethyl alcohol and acetaldehyde efficiencies increases up to 300°C, above this point they tends to decrease and this effect can be attributed to the fact that, at high temperatures high degree of hydrocracking reaction occurs and formation of various by-products may occurs. Temperature increase gives a sufficient energy for desirable and undesirable reaction to proceed. Selectivity of the catalyst will limits the undesirable reaction to an extent depend on the goodness of the catalyst design.

A decrease in ultimate yield, and the efficiencies are also recorded in previous work, as a results of high temperature and low LHSV (Toussaint, Corson). The definition and calculations of two-step per pass, ultimate yields, ethyl and acetaldehyde efficiencies are outlined below. The factor 0.92 in the ultimate yield formula was used in conformance with plant practice, the ultimate yield of the dehydrogenation of ethyl alcohol being 92%. The ultimate butadiene yield was therefore based on the overall ethyl alcohol consumption. The factor was omitted in calculating the per pass yield, again to conform with plant practice.

## CONCLUSIONS

1. Within the studied range, catalyst bed temperature and LHSV strongly affect the butadiene yields and selectivitis in one and two-step process.
2. 80%MgO:20%$SiO_2$ catalyst gave good butadiene yields and selectivities. At 350°C and 0.5 $h^{-1}$, the first prepared catalyst gave per pass yield and ultimate yield 12.2 mole% and 26 mole% respectively.
3. Butadiene yield increases as the temperature increases, while the selectivities decreases at high temperatures and low LHSV.
4. The optimum ethyl alcohol to acetaldehyde mole ratio was a function of temperature, 2.76:1 ratio being the optimum at 400°C (41.5% ultimate yield), 3:1 ratio at 350°C (39.7% ultimate yield), and 1.5:1-3:1 ratio at 250-300°C (33.2%-36.8% ultimate yield).

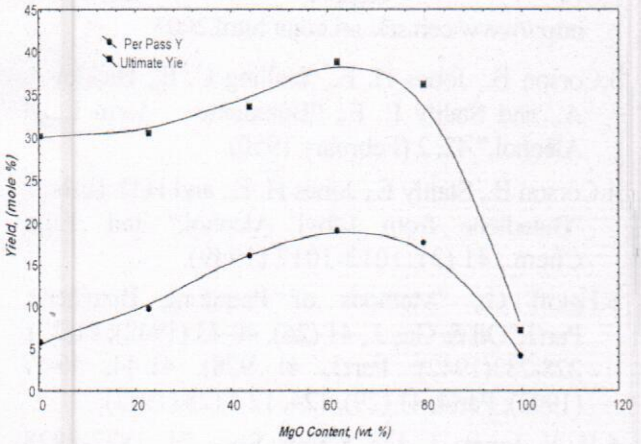


Figure (2) Effect of MgO Content in MgO:SiO$_2$ Catalyst on Butadiene Per Pass and Ultimate Yields at 0.47 LHSV and 350°C.

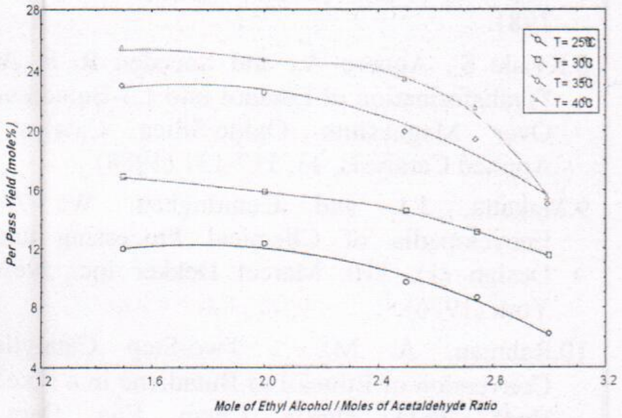


Figure (3) Effect of Ethyl alcohol to Acetaldehyde Mole Ratio on Butadiene Per Pass Yield at Various Temperatures Using 80%MgO:20%SiO$_2$ Prepared Catalyst

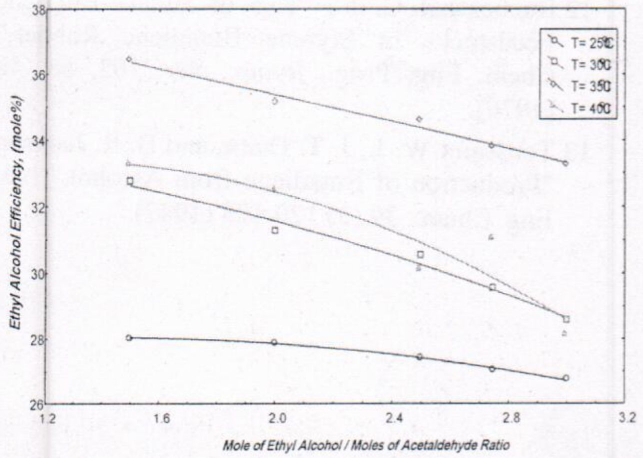


Figure (4) Effect of Ethyl Alcohol to Acetaldehyde Mole Ratio on Ethyl Alcohol Efficiency at Various Temperatures Using 80%MgO:20%SiO$_2$ Prepared Catalyst

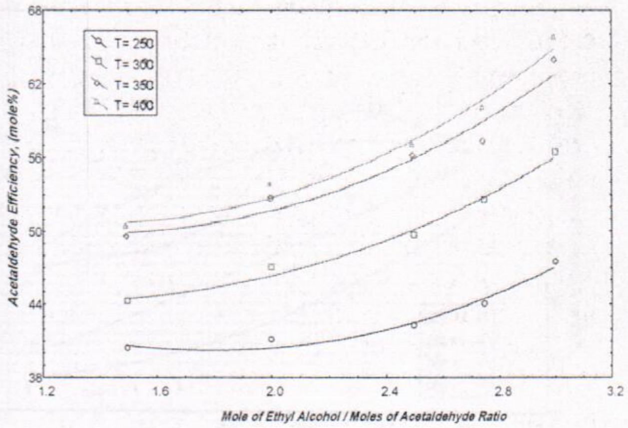


Figure (5) Effect of Ethyl Alcohol to Acetaldehyde Mole Ratio on Acetaldehyde Efficiency at Various Temperatures Using 80%MgO:20%SiO$_2$ Prepared Catalyst.

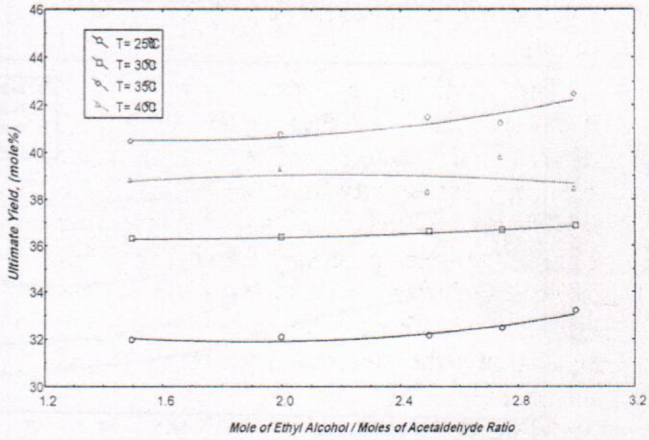


Figure (6) Effect of Ethyl Alcohol to Acetaldehyde Mole Ratio on Butadiene Ultimate Yield at Various Temperatures Using 80%MgO:20%SiO$_2$ Prepared Catalyst.

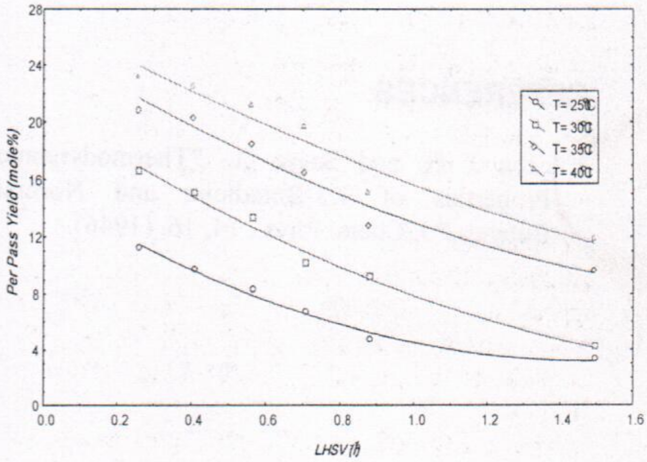


Figure (7) Effect of LHSV on Butadiene Per Pass Yield at Various Temperatures Using 80%MgO:20%SiO$_2$ Prepared Catalyst.

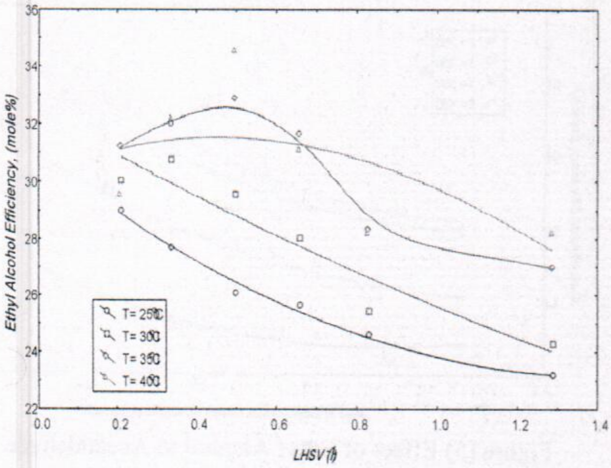


Figure (8) Effect of LHSV on Ethyl Alcohol Efficiency at Various Temperatures Using 80%MgO:20%$SiO_2$ Prepared Catalyst.

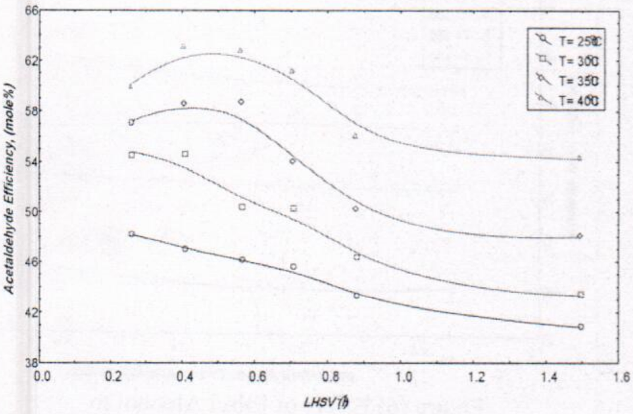


Figure (9) Effect of LHSV on Acetaldehyde Efficiency at Various Temperatures Using 80%MgO:20%$SiO_2$ Prepared Catalyst.

## REFERENCES

1.Aston J. G. and Szasz G., "Thermodynamic Properties of 1,3-Butadiene and Normal Butenes," J. Chem. Phys., 14, 16, (1946).

2.CEP Report- Butadiene, http://www.ceh.sric.sri.com/ html.2003

3.Corson B., Jones H. E., Welling C. E., Hickley J. A., and Stahly E. E., "Butadiene form Ethyl Alcohol," 42, 2 (February 1950).

4.Corson B., Stahly E., Jones H. E., and H.D. Bishop, "Butadiene from Ethyl Alcohol," Ind. Eng. Chem., 41 (3), 1012-1017 (1949).

5.Egloff G., "Methods of Preparing Butadiene, Part1,"Oil & Gas J., 41 (26), 40-43 (1942); 41(27), 228-233(1942); Part3, 41 928), 41-44, 46-47 (1942); Part4, 41 (29), 124, 127-128 (1942).

6.H. E. Jones, J. Am. Chem. Soc., 71, 1822-1828 (1949).

7.International Standard ISO 6378, "Butadiene for Industrial Use- Determination of Hydrocarbon Impurities- Gas Chromatography Method," 1981.

8.Kvisle S., Aguero A., and Sneeden R. P. A. "Transformation of Ethanol into 1,3-Butadiene Over Magnesium Oxide/Silica Catalyst," Applied Catalysis, 43, 117-131 (1988).

9.Maketta, J.J. and Cunningham W. A., Encyclopedia of Chemical Processing and Design (1), 110, Marcel Dekker Inc., New York (1976).

10.Rahman, A. M., " Two-Step Catalytic Conversion of Ethanol to Butadiene in a Fixed Bed", Ph.D. Thesis, Chem. Eng. Dept., Baghdad University (2004).

11.Ramsey G. S., "Butadiene and Nitrile Rubber ," Chem. Eng. Prog., Symp. Ser. 103, 66, 57 (1970).

12.Ruebensaal C. F., "Use of Butane-Butylene Feedstocks in Styrene Butadiene Rubber," Chem. Eng. Prog., Symp., Ser. 103, 66, 40 (1970).

13.Toussaint W. J., J. T. Dunn, and D. R. Jackson "Production of Butadiene from Alcohol," Ind. Eng. Chem., 39 (2) 120-125 (1947).