PRODUCTION OF METHYL ETHYL KETONE FROM N-BUTANE

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ABSTRACT

The aim of this research is to produce MEK from oil products. For this purpose the following steps were taken:

1- n-butane was selected as a feed.

2- A production process of four steps were applied. These are:

2-1-Pyrolysis and dehydrogenatiion of n-butane.

2-2-Sulfation of n-butenes.

2-3-Hydrolysis of the butyl sulfate.

2-4-Dehydrogenation of secondary butanol.

3- A pilot plant was designed and builds to comprised the above stages. It has the following properties:

3-1-The possibility of operation over wide ranges of conditions on a variety of systems employing solid catalysts.

3-2-Operation can be either as an "integral reactor" to simulate the results of a "commercial reactor" for the direct determination of absolute reaction rate.

4- 57% conversion of secondary butanol to MEK was obtained at (constant operating conditions). Height conversion could be reached by reducing space velocity.

5- The intermediate products [n-butenes, and 2-butanol] were also produced. Catalytic dehydrogenation was selected as a source of n-butenes with yield of 35% and sulfation of butenes subsequent hydrolysis to 2-butanol was also carried out with conversion of 88%.

INTRODUCTION

There are two principal sources of olefins from petroleum, namely: separation from olefins rich gases from refinery operations, and separation from mixed gases obtained from pyrolysis and catalytic units operated for the prime purpose of producing olefins either from natural gas or crude oil.

The butylenes obtained from the dehydrogenation of C_4 are used as raw materials in the manufacture of a variety of products such as synthetic rubber, alkylation products and solvents including methyl ethyl ketone (MEK). Methyl ethyl ketone (MEK) is an important commercial chemical that is produced in large quantities for a wide variety of processes and products[1,2,3,4,5,6,7,8,9] It is used as a solvent for lubricating oil refining. The MEK selectivity dissolves the oil from the wax. It is also used as a reaction solvent in one of the terephthalic acid processes.

It is a powerful solvent, only partially miscible in water, has a lower vapor pressure and correspondingly higher boiling point than acetone and these properties are exploited in the synthesis of various compounds, such as surface coating, antiskinning agents as methyl ethyl ketoxime, cellulose manufactures, acrylic resin, polyester and vinyl polymer production as polymerization catalyst, as methyl ethyl ketone peroxide, and corrosion inhibitor as methyl pentynol.

In fact nearly all synthetic resins commonly employed in lacquers are soluble in MEK and furthermore it is employed as a solvent in many extraction processes in the chemical and petroleum industries. MEK undergoes a number of special reactions such as condensation with aldehydes to form high molecular weight ketones, cyclic compounds and ketals.

There are five methods for manufacture of KEK[1,2,4,5,10,11,12,13,14,15,16,17,18]. These are: (1) Synthesis from refinery gases. (2) Dehydrogenation from 2-butanol (sec-butyl alcohol). (3) Selective oxidation of 2-butanol. (4) From n-butenes by liquid phase Wacker-type process. In Europe a liquid phase process uses

Raney nickle, or copper chromite as the dehydrogenation catalyst at 150°C. (5) Liquid phase oxidation (LPO) of n-butane to produce mainly MEK at reactor specification of L/D>10,000 otherwise acetic acid is the major product.

The most popular process being the dehydrogenation of sec-butanol, about 90% of sec-butanol production is converted to MEK[1]. The sec-butanol being obtained from butenes which in turn is obtained from starting raw material (other than butane) include LPG, naphtha, reformer raffinate, gas oil, and kerosene. The preparation of MEK starting from butane gas, involves the following operations. (1) Dehydrogenation of butane to produce olefins mainly ethylene, propylene and butenes (butylenes). The extent of each product depends generally on the operating temperature and the selectivity of the catalyst. Recycling the butane gives high yields. (2) Sulfation of the olefins using sulphuric acid to produce sulfates of olefins. (3) Hydrolysis of the sulfation products to produce alcohols such as ethanol, iso-propanol, and sec-butanol. These alcohols are separated by distillation for their various subsequent uses. (4) dehydrogenation of sec-butanol to produce MEK. In this operation, as well as in the first one, hydrogen is obtained as a byproduct which may be used as a fuel.

Catalytic Dehydrogenation

Gaseous paraffins are dehydrogenated at atmospheric pressure in the presence of a suitable catalyst such as chromic-oxide gel or chromium oxide on alumina at temperature of 350°C to 750°C[19,20,21,22].

$$C_nH_{2n+2} \rightarrow C_nH_{2n} + H_2$$
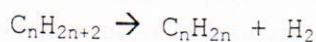
Catalytic dehydrogenation of n-butane, iso-butane, and propane to the corresponding olefins is a highly selective reaction and produces, on a commercial scale 85 to 95 percent of theoretical yield of olefins from paraffins. Actually, in the laboratory on a recycle basis, more than 95 percent of theoretical yield of the olefins from paraffins has been obtained.

The catalytic reaction suppresses the occurrence of side reaction, such as the formation of methane, and ethane from propane and butane. Also, when processing butanes, it suppresses propane formation and produces principally butenes[19].

Sulfation of Butenes

The conversion of olefins to alcohols involves merely reaction with sulfuric acid to form definite chemical compounds which are simultaneously, or more often later, hydrolized to give alcohols. Sulfuric acid[2,23], is the only reagent now used industrially for the conversion of olefins to alcohols. Other reagents of an acid character have been proposed, but for various reasons (mostly poor yield) they are not used.

In general[24,25], the primary reaction of sulfuric acid with the lower mono-olefins results in the formation of the corresponding acid sulfate ester or alkylsulfuric acid. Thus,

$$C_nH_{2n} + H_2SO_4 = C_nH_{2n+1}HSO_4 \qquad (1)$$
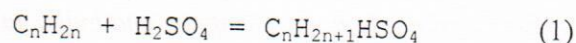
Or more explicitly,

$$C_nH_{2n} + HSO_4^- = C_nH_{2n+2}SO_4^- \qquad (2)$$
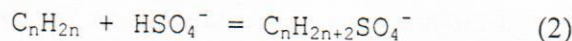
However, the ester may subsequently react with other constituents of the reaction mixture – the excess sulfuric acid, the olefin, or water, if present – or with itself; the direction and extent of these reactions depend on such conditions as the constitution, molecular weight, and concentration of the olefins, the concentration of the acid, and the temprature.

Hydrolysis of Sulfation Products

Alkyl sulfates are fairly stable in the presence of water at ordinary temperatures. On heating with water, they are readily hydrolized and this hydrolysis is promoted by hydrogen ion. It was found in a special laboratory studies of 2-butyl, isopropyl alcohols manufacture, the mono-alkyl sulfates are most stable in excess caustic alkali solution and may be boiled in such solutions with only very slow hydrolysis, but in acid solution the hydrolysis is increasing rapid with increasing acid concentration.

The fact that alcohol is not readily removed under ordinary conditions without dilution of the extract is explained by the presence of alcohol in the form an ion, which called the aloxonium ion. The aloxonium ion is readily decomposed by the addition of water, however to liberate the alcohol in the proton exchange reaction.

$$ROH_2^+ + H_2O = ROH + H_3O^+ \qquad (3)$$
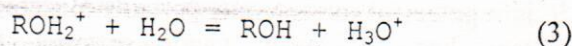
Dehydrogenation of Secondary Butanol

The most famous method of MEK production is the vapor catalytic dehydrogenation of 2-butanol[26,27,28,29,30]. Zinc oxide or brass are commonly used as catalyst. The optimum reaction temperature of 400-550°C should be maintained. Expected conversion of 75 percent should be controlled to minimized catalyst coking.

EXPERIMENTAL FLOW DESCRIPTION FOR MEK PRODUCTION

The flow plan of the pilot as arranged for MEK production is shown in figures (1,2, and 3). Cylinder of liquefied hydrocarbon gas C_1 to C_5 are arranged in such away to draw off gas of uniform composition. A pressure regulator was used to maintain the hydrocarbon charge pressure at the desired limit. The hydrocarbon feed rate was indicated and controlled by means of calibrated gas rotameter, and thoroughly dried before entering the reactor. Pressure and temperature measuring devices were installed before and after the reactor chamber.

The isothermal reactor was surrounded by an electrical tubular furnace in order to reach the desired reaction temperature. The reaction product was then passed directly through the surge tube which was surrounded by cooling water coil to supress the reversible reactions. Suitable concentrations were located before and after the reaction chamber to draw off samples at predetermined intervals during the process period in order to show the change in catalyst activity as the run progress, and also to analyze the hydrocarbon gases resulted from reaction.

Samples of the gases leaving the reaction zone were automatically analyzed (connection on line) or manually collected and analyzed in gas-liquid chromatography unit type (CHROMPAK). C_1 to C_6 hydrocarbon gases could be qualitatively and quantitatively determined.

To reach the feed temperature of the next stage (sulfation process), and the desired column temperature of the gas-liquid chromatography several cooling was required. This was attained by using a cooling box. Reaction products were passed through a calibrated gas rotameter, in order to be ready to feed to the next stage, and also to determine the gas expansion, which is an important factor in the design scale-up. Provision was made for introducing into reaction zone, as

required, hydrocarbon feed, nitrogen for purging, air for regeneration and hydrogen for reduction.

The adiabatic dehydrogenation process requirements was attained by employing a preheat system – Figure (2). It consists of a standard steel pipe (ASTM316-SUS) 6.3mm in diameter and 5550mm in long, which was of a spiral shape. The diameter and number of turns were 60mm, and 31 respectively. All connections were sealed to prevent any leakage of air to the reaction chamber during operation which may cause explosion.

The experiment plan for olefin sulfation in Figure (3). Gases from dehydrogenation stage were metered in calibrated gas rotameter. Olefin gases (including n-butane) passed through gas distributor to be in contact with 80 percent sulfuric acid at 1.6 atm and about 20-26°C. The acid reacts with olefins to form olefin sulfate (e.g. butyl sulfates). Reaction conditions were kept fixed by adjustment of cooling water flow rate.

The parameter measured were: feed flow rate, residual gases, flow rate, pH, temperature and time of reaction. Residual paraffins (butane) was removed from the product in a phase separator and the acid-sulfate mixture was sent to the hydrolysis stage. Hydrolysis of the product was attained by mixing each one volume of sulfated product with three volume of distilled water. Cooling the mixture was necessary at the beginning to keep the sulfate stable.

The flow plan of the 2-butanol dehydrogenation is as shown in Figure (4). Amount of cold feed (2-butanol) was placed in a graduated funnel. The funnel was connected to the evaporator by a plastic tube provided with a valve. Preheated vapor from evaporator was then passed through a mist (or drops) accumulator in order to draw off any entered liquid that might be separated from vapor stream.

In order to meet the reaction temperature, the alcohol vapor was superheated by employing a 6.3mm, or ¼ inch in diameter of a standard steel coil (specification of this coil was mentioned above) which was fixed inside the tubular furnace. The superheated alcohol then passed through the vertical stainless steel reactor. The reaction temperature was measured by using a thermocouple of type J, which was fixed longitudinally at the center of the reactor.

Reaction products discharge from this reactor consisted of MEK vapor, hydrogen, and unchanged alcohol. All these products are reasonably stable below 400°C, so that it is

unnecessary to install a rapid quench unit. The reaction products then passed through an efficient water condenser, where most of the MEK and

alcohol were condensed and collected in a suitable receiver, while the remainder (saturated vapor in the on-condensable hydrogen) was vented off.
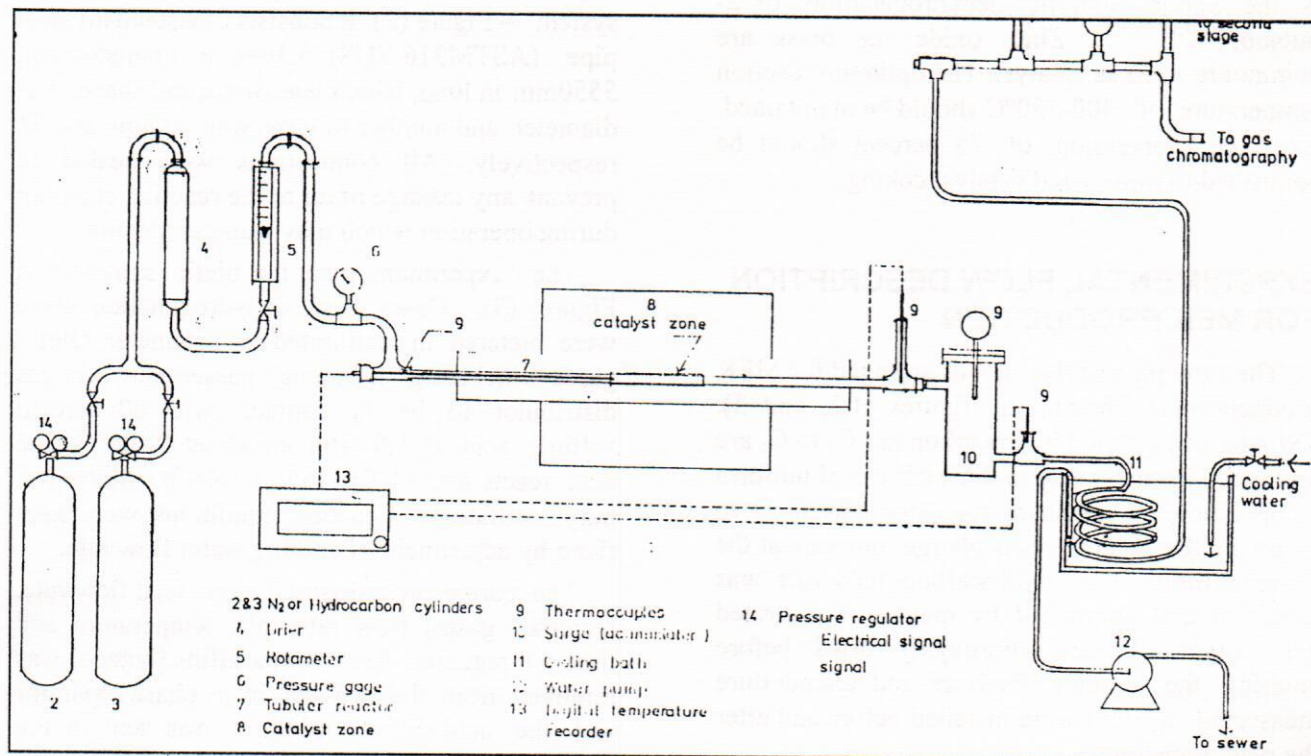
Figure (1) Flow plan of hydrocarbon gas dehydrogenation (isothermal)

2&3	N₂ or Hydrocarbon cylinders	9	Thermocouples	14	Pressure regulator
4	Drier	10	Surge (accumulator)		Electrical signal
5	Rotameter	11	Cooling bath		signal
6	Pressure gage	12	Water pump		
7	Tubular reactor	13	Digital temperature		
8	Catalyst zone		recorder		
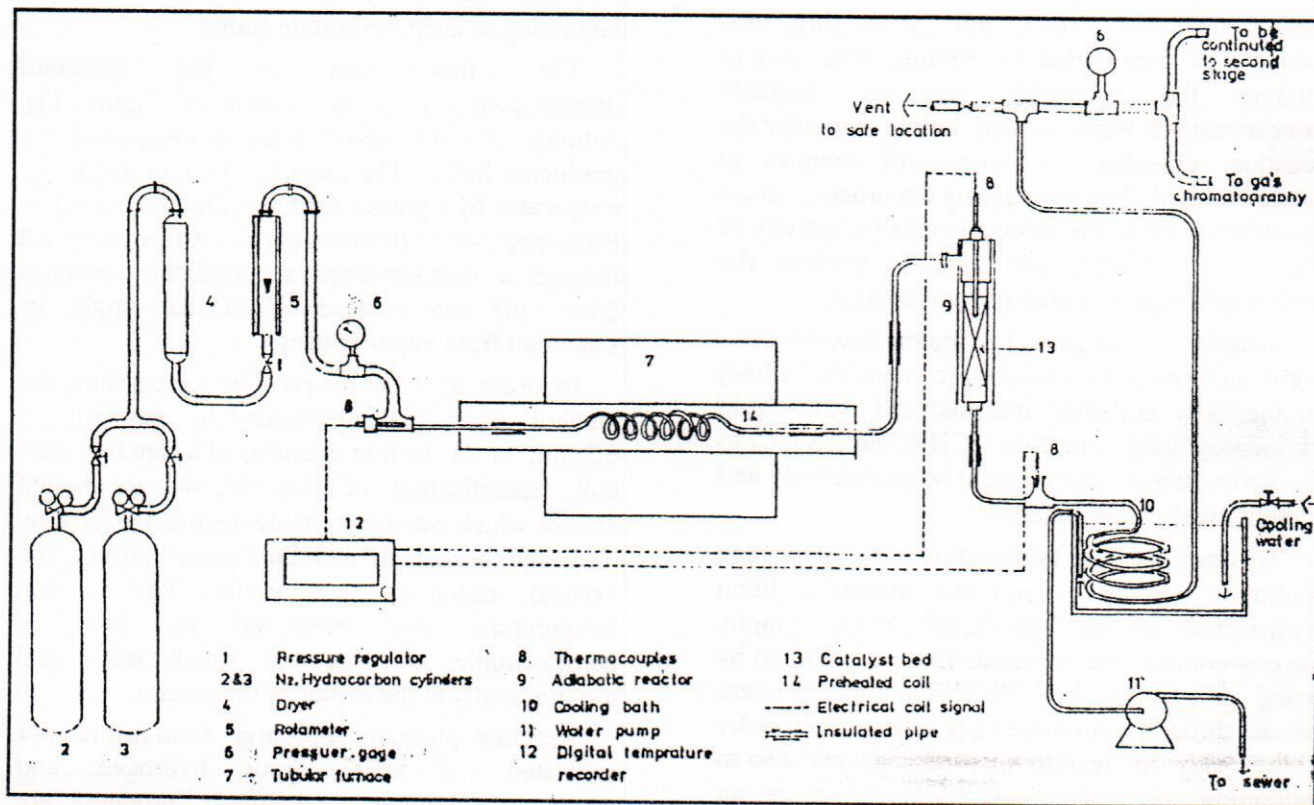
Figure (2) Flow plan hydrocarbon gas dehydrogenation (adiabatic)

1	Pressure regulator	8.	Thermocouples	13	Catalyst bed
2&3	N₂, Hydrocarbon cylinders	9	Adiabatic reactor	14	Preheated coil
4	Dryer	10	Cooling bath	-----	Electrical coil signal
5	Rotameter	11	Water pump		Insulated pipe
6	Pressure gage	12	Digital temprature		
7	Tubular furnace		recorder		

1 - Rotameter.
2 - Distributor.
3 - Cooling water coil.
4 - Contact tower
5 - Mixter
6 - P H - meter electrod
7 - Thermometer
8 - Electrical motor
9 - Phase seperator
10 & 11 - Distilled water & sulfate solution conbines
12 - Mixing branch
13 - Hydrolyzer
14 - Treating vessel
15 - Sample point
16 - Plt - meter

Figure (3) Sulfation and hydrolysis plan

1	Round flask	9	Thermometer
2	Gas rotumeter	10	Recievir
3	Pressure gouges	11	Preheated coil
4	Thennocouple type T	12	Sampling gus collecter
5	Tubular furnace	13	Temp-recorder
6	Stainless steel pipe	14	Graduated cylinder
7	Thermocouple	15	Adiabatic reactor
8	Condenser	16	Heater
		17	Catalyst bed

------- Electrical signal
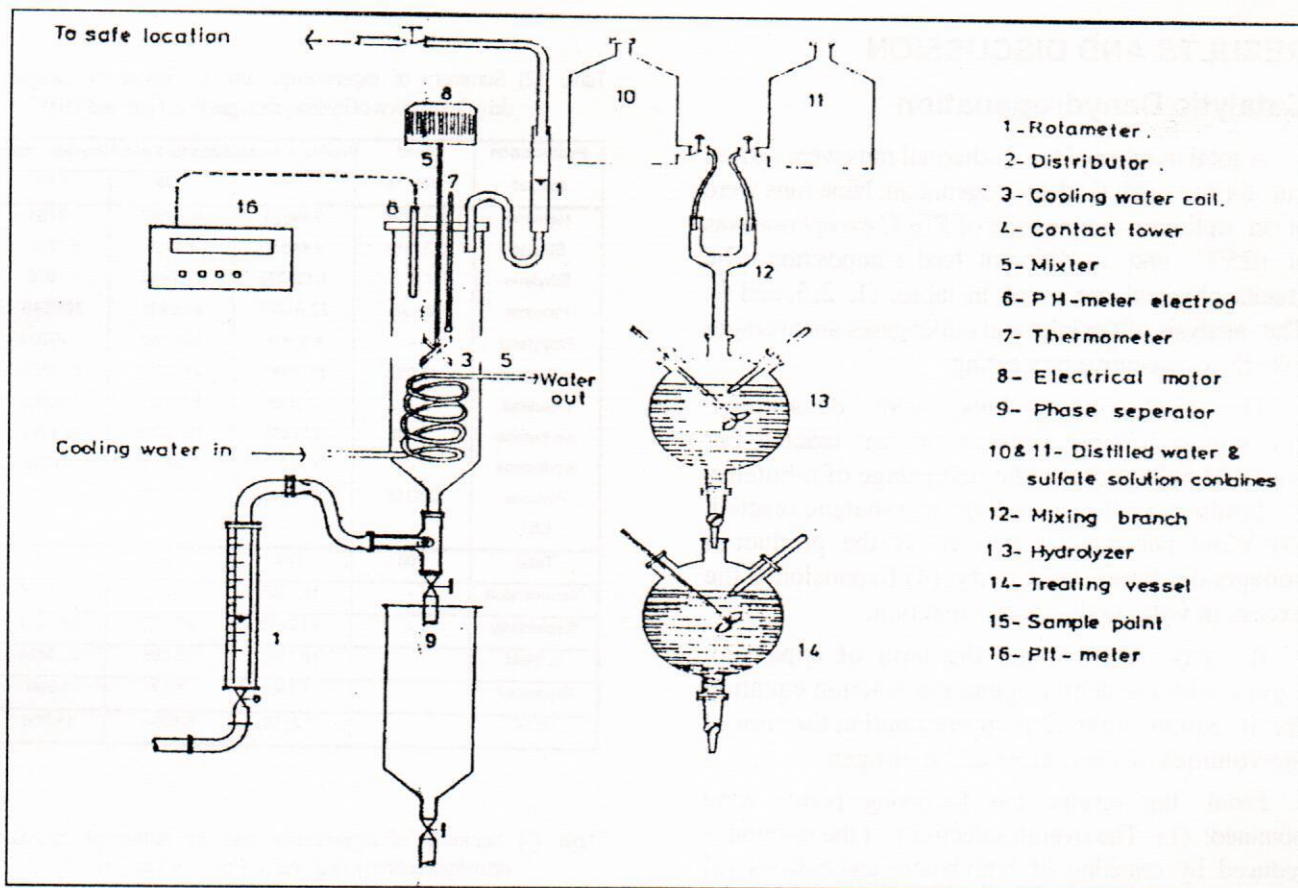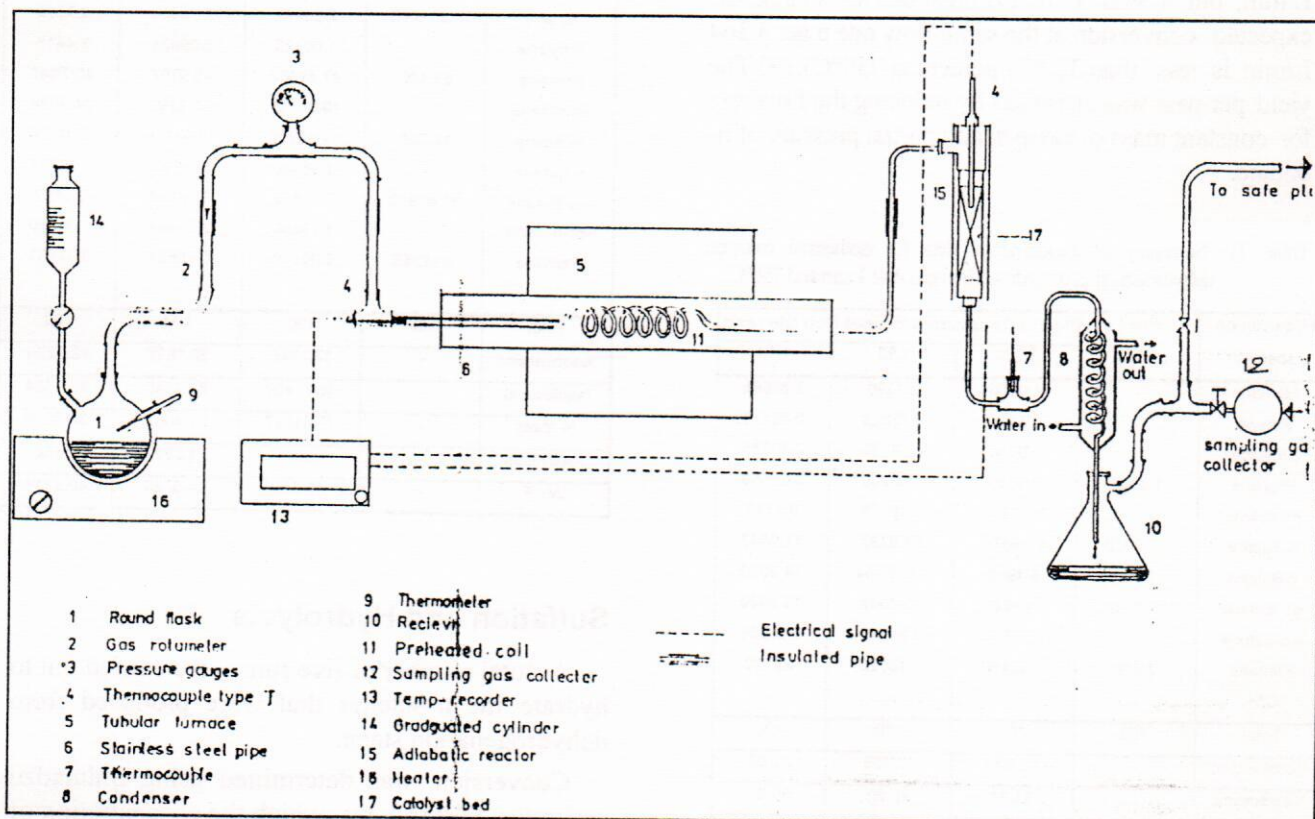⟶ Insulated pipe

Figure (4) The flow plan of 2-butanol dehydrogenation

RESULTS AND DISCUSSION

Catalytic Dehydrogenation

A total number of ten isothermal runs were carried out for the catalytic dehydrogenation. Nine runs were at an optimum temperature of 570°C except one was at 625°C, and at different feed composition. The results obtained are given in tables (1, 2, 3, and 4). The analysis of the inlet and outlet gases are averages over the consecutive processing.

The following values were determined: (1) conversion per pass or percent reacted per pass. (2) Selectivity in the percentage of n-butenes in product per the percentage of n-butane reacted. (3) Yield per pass is defined as the product of conversion times selectivity. (4) Expansion is the excess in volume due to the reaction.

It may be seen that the term of expansion agrees with the dehydrogenation reaction equation for it equals in the first approximation the sum of the volumes of the olefins and hydrogen.

From the results, the following points were obtained: (1) The overall selectivity of the reaction is reduced by cracking of both butane and butenes. (2) The conversion is increased from 32.474 percent to 67.754 percent by increasing the temperature from 570°C to 625°C (the flow rate at 570°C was 2.3748 L/min, but it was 3.364 L/min at 625°C. So that, the expected conversion at the same flow rate e.ge. 3.364 L/min is less than 32.474 percent at 750°C). (3) The yield per pass was increased by reducing the flow rate for constant mass of catalyst and partial pressure of n-butane.

Table (1) Summary of experimental data for isothermal catalytic dehydrogenation of hydrocarbon gas A at 1 atm and 750°C.

Hydrocarbon species	Feed Mole %	Product Compositions for Feed Flow rate l /min		
		2.374	1.80	1.10
Methane	-	1.0170	2.1290	2.23895
Ethane	-	0.8926	0.72628	0.86113
Ethylene	-	0.9230	0.76159	0.90265
Propane	1.2335	0.9860	0.96200	0.87559
Propylene	-	0.21300	0.19226	0.1750
n-Butane	77.2835	67.9870	64.0382	61.0543
n-Butene	-	8.4980	11.79144	14.3000
iso-Butane	17.8128	14.4283	13.6542	13.3600
iso-Butene	-	3.21500	3.57800	4.36350
Pentane	3.670	1.83400	2.16720	1.8720
C5+	-	-	-	-
Total	100	100	100	100
%conversion	-	12.030	17.138	21.00
%selectivity	-	91.41	90.80	88.01
% Yield	-	11.00	15.25	18.50
Expansion	-	1.128	1.175	1.22
W/F	-	4.2658	7.2823	9.2095

Table (2) Summary of experimental data for isothermal catalytic dehydrogenation of hydrocarbon gas B at 1 atm and 750°C.

Hydrocarbon species	Feed Mole %	Product Compositions for Feed Flow rate l /min		
		2.374	1.80	1.10
Methane	0.17296	0.86678	1.02367	1.4761
Ethane	3.31474	3.44867	3.4925	3.7777
Ethylene	-	1.135233	1.27413	1.7870
Propane	26.32	22.01377	21.6456	20.6548
Propylene	-	4.97470	5.04150	6.30200
n-Butane	45.057	36.80863	35.7243	30.5825
n-Butene	-	7.3585	9.13955	12.23300
iso-Butane	21.40	17.7590	17.18218	16.1391
iso-Butene	-	3.18213	3.6819	4.4700
Pentane	3.6115	2.85255	2.79100	2.5784
C5+	-	-	-	-
Total	100	100	100	100
%conversion	-	18.3065	20.713	32.1248
%selectivity	-	89.2115	87.153	84.5141
% Yield	-	16.3315	18.065	27.1434
Expansion	-	1.190	1.22	1.280
W/F	-	7.3170	9.6534	15.800

Table (3) Summary of experimental data for isothermal catalytic dehydrogenation of hydrocarbon gas C at 1 atm and 750°C.

Hydrocarbon species	Feed Mole %	Product Compositions for Feed Flow rate l /min		
		2.374	1.80	1.10
Methane	0.0059915	1.38227	1.96876	2.0721
Ethane	1.311748	2.23582	2.70938	2.7399
Ethylene	-	1.69129	2.29031	2.4415
Propane	69.400	47.49952	43.9791	40.7647
Propylene	-	19.38135	21.8360	24.9888
n-Butane	17.700	11.95209	10.94166	10.10280
n-Butene	-	4.86930	5.5590	6.15658
iso-Butane	11.40213	7.75632	7.10538	6.6082
iso-Butene	-	3.13660	3.52434	4.04520
Pentane	0.42358	0.09540	0.08651	0.07981
C5+	-	-	-	-
Total	100	100	100	100
%conversion	-	32.4740	38.1827	42.9220
%selectivity	-	84.71427	82.2540	81.0364
% Yield	-	27.51017	31.4067	34.7830
Expansion	-	1.335	1.386	1.438
W/F	-	18.626	24.5738	40.2119

Sulfation and Hydrolysis

A total number of five runs were carried out to hydrate the n-butenes that were produced from dehydrogenation stage.

Conversion was determined using Shimadzu separator UV-160 by which the concentration of 2-butanol after hydrolysis with distilled water was obtained. See table (5).

Table (4) Summary of experimental data for isothermal catalytic dehydrogenation of hydrocarbon gas B at 1 atm and 625°C.

Hydrocarbon species	Feed Mole %	Product Compositions
Methane	0.0059915	0.33844
Ethane	1.311748	0.20717
Ethylene	-	2.158068
Propane	69.400	31.7798
Propylene	-	49.9006
n-Butane	17.700	5.70750
n-Butene	-	5.441828
iso-Butane	11.40213	2.64680
iso-Butene	-	1.31268
Pentane	0.142358	0.5067
C5+	-	-
Total	100	100
%conversion	-	67.7542
%selectivity	-	45.377
% Yield	-	30.74428
Expansion	-	1.624
Flow rate l/min	3.364	5.470
W / F	13.6789	-

Table (6) Summary of experimental data of secondary butanol dehydrogenation

RUN	1	2	3	4	5	6
Flow Rate liquid (l/min)	0035	0.081	0.06335	0.0238	0.0441	0.0263
Flow Rate liquid kg/h	1.6884	3.907	3.056	1.1514	2.1273	1.270
Flow Rate Vapour l/min.	6.228	14.406	11.261	4.240	7.876	4.710
%Conversion	37	27	31	57	40	53.85
p_B (atm.)	0.4598	0.5746	0.5267	0.2738	0.4285	0.2999
p_K or p_H (atm.)	0.2700	0.2125	0.2366	0.3630	0.2857	0.3500
Space velocity 1/h.	13939	32242	25203	9489	17627	10541
W/F kcal/m^3/min	13.327	3.6790	4.706	12.500	6.73	11.25
Rate of Reaction g.mol/h.m^2	5.286×10^{-4}	6.093×10^{-4}	5.726×10^{-4}	3.964×10^{-4}	5.010×10^{-4}	4.074×10^{-4}
Rate of Reaction kg.mol /s.g.cat.	0.00424	0.00488	0.004592	0.00317	0.0040	0.00326

Table (5) Experimental runs of n-butenes sulfation. Run time 2.7 hr/batch vol. 230cc

Temperature °C.	%Conversion of H_2SO_4	Olefin gas flow rate g./s.
22	72.4	0.0114
22	72.76	0.01146
20	71.04	0.01118
26	88.01	0.01386
24	74.63	0.01175

Table (7) Effect of space velocity and W/F on conversion

%conversion	Space Velocity 1/h.	W/F kg.catalyst.J/(m3/min.)
27.00	32242	36790
53.85	10541	11.250
57	9489	12.500

Dehydrogenation of 2-butanol

A total number of six adiabatic runs were carried out for the vapor phase dehydrogenation of secondary butanol.

The results obtained from the catalytic dehydrogenation of secondary butanol are given in Table (6), Figure (5, and 6) illustrating the influence of space velocity and the ratio of mass of catalyst to flow rate on percent of conversion at operating temperature of 450°C. It can be seen that the percent of dehydrogenation of secondary-butanol is increased by 99-99.4 percent by reducing the space velocity or increasing the ratio of W/F by 67-70 percent. See table (7).
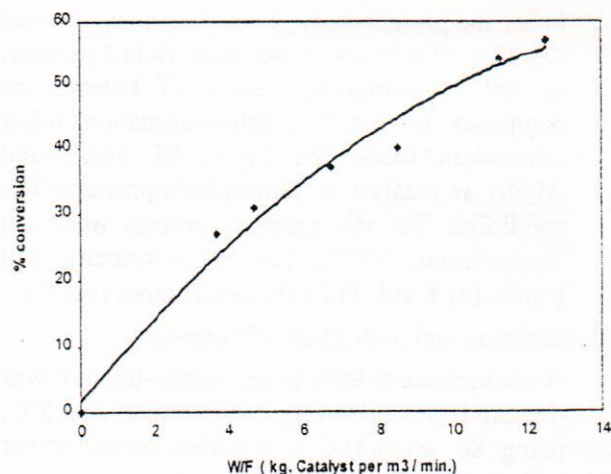

Figure (5) Relationship between percent conversion to MEK and W/F
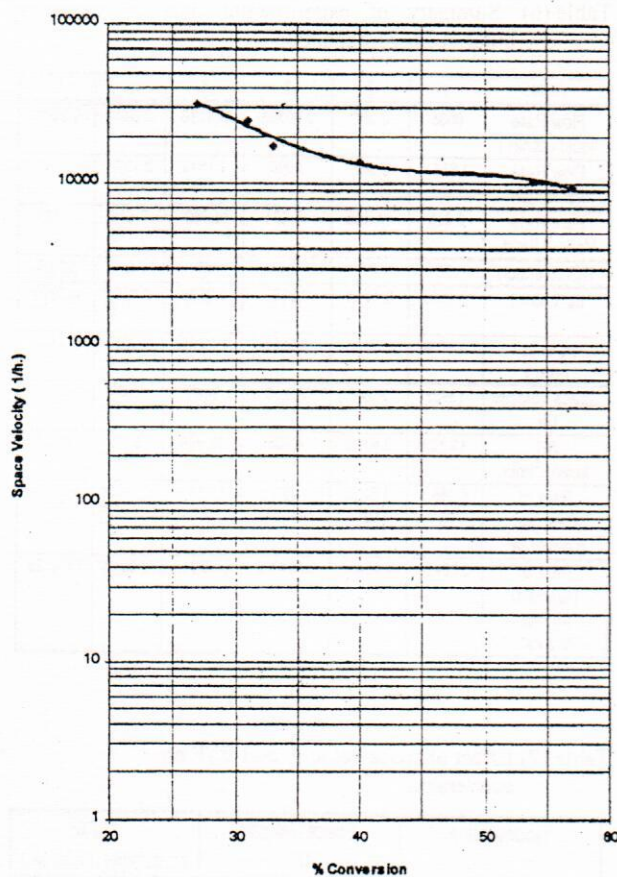
Figure (6) Relationship between space velocity and percent conversion.

CONCLUSIONS

1. Dehydrogenation of n-butane:

From the present study, it was found that thermal cracking of n-butane, (maximum yield 3 percent) is not a competing source of butenes, as compared to catalytic dehydrogenation, using (chromium oxide 9% Cr_2O_3, 89 Fe_2O_3, and Al_2O_3) as catalyst as atmospheric pressure. The conditions for the catalytic process were: (a) Temperature, 570°C, (b) Space velocity, 950 L/min, (c) Yield, 34.783% of n-butenes (gas C).

2. Sulfation and hydrolysis of butenes:

A conversion of 88% to secondary-butanol was obtained at operating temperature of 25°C, using 80 wt.% H_2SO_4 in bubble contact tower and semibatch operation.

3. Dehydrogenation of secondary butanol:

It was carried out at an average operating temperature of 450°C, with space velocity of 9489 L/hr, the conversion was 57% to MEK using zinc oxide. (95% Zn, 3% Al_2O_3, As<1 ppm) as catalyst under adiabatic conditions at one atmosphere.

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