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Direct Hydration of Olefins

. . . *with Cation Exchange Resins*

This method, coupled with dehydration, provides an economical means of preparing pure alcohols or pure iso-olefins from refinery streams

THE use of ion exchange resins as catalysts has received considerable attention as a means of advantageously effecting various chemical conversions. For example, resin catalysts have been used in epoxide formation, ethylene oxide hydrolysis, ester formation, and many other reactions. These and other applications have been covered in review articles (*1*, *3*).

No study on the use of cation exchange resins for the selective hydration of branched olefins or selective dehydration of tertiary alcohols has been reported to date. The nonselective dehydration of pure alcohols has been reported, however (*4*), as well as data on the hydration of pure isobutylene (2-methylpropene) with a sulfonated coal (*2*) and an ion exchange resin (*5*).

This investigation was undertaken to determine the applicability of sulfonated polystyrene-divinylbenzene resins as catalysts for the selective hydration of branched olefins as a means of obtaining valuable alcohols and, by subsequent dehydration, pure iso-olefins.

It was found that ion exchange resin catalysts are indeed effective for the selective direct hydration of the iso-olefins present in C_4-C_5 refinery streams at moderate temperatures and pressures. High purity iso-olefins can be recovered either by dehydration of pure tertiary alcohols or by selective hydration (at proper conditions) of the tertiary alcohol in tertiary-secondary-primary alcohol mixtures. Thus, a simple process can be used to prepare tertiary alcohols and/or pure iso-olefins from C_4-C_5 refinery streams.

Experimental

Equipment. All continuous-flow hydration experiments were made in a reactor of 2-inch, Schedule 80, stainless steel pipe, 11 inches long with an internal volume of 500 cc. The reactor was heated by an electric furnace equipped with two manually controlled heaters. Catalyst temperatures were measured by three thermocouples inserted in a central thermowell.

A Hills-McCanna pump was used for both hydrocarbon and water feed. The mixed butane-butene stream was pumped as a liquid directly from a high pressure reservoir, while the mixed C_5 stream was pumped from a refrigerated glass buret. In both cases, hydrocarbon feed was joined with water feed preceding a coil preheater just prior to entering the reactor. The reactor effluent went to a cooler, through a pressure-control valve, and to a low-pressure receiver from which the liquid product was recovered. Unconverted feed was vented from the receiver to a gas meter and sampling system.

Batch hydration experiments were made in a standard, 1800-cc. shaker bomb (American Instrument Co.). Atmospheric pressure dehydration experiments were made downflow in a conventional borosilicate glass reactor of 90-cc. catalyst volume. Feed rate was controlled by a bellows pump (Research Appliance Co.) from a water-jacketed glass buret.

Procedure. In pressure flow experiments, IR-120 resin catalyst (Rohm & Haas) was protonated prior to use by contacting for 15 to 30 minutes with an 18% solution of HCl. The resin was then washed with distilled water until free of chloride ion ($AgNO_3$ test) and dried at 250° F. When charging the reactor, 250 cc. of the dry resin was saturated with water, expanding it to the volume of the reactor.

After saturating the catalyst, the system was brought to operating pressure with nitrogen, and heat was applied to the reactor. The mixed feed was started and the operating temperature lined out during an off-stream period, usually about 2 hours. At uniform operating conditions, data were collected for a 4-hour test period.

Operating pressure was maintained at about 25 p.s.i.g. above feed saturation pressure to ensure liquid phase operation. Little external heat was required on the reactor, after lined-out conditions had been reached, since the heat of reaction was usually sufficient to maintain operating temperature. All space velocities and throughputs were based on the volume of dry resin charged to the reactor. Upon wetting, the dry volume approximately doubled, so actual space velocities are about one half those reported.

Analysis. Initially, the yield of *tert*-butyl alcohol (2-methyl-2-propanol) obtained from hydration of the butane-butene stream was determined by distillation to obtain the water-alcohol azeotrope. However, the absence of side reactions, as later determined by infrared analysis, enabled simplified yield determination by the use of a refractive index *vs.* alcohol-water composition diagram. The *tert*-amyl alcohol (2-methyl-2-butanol) obtained from hydration of methylbutenes was determined by mass spectrometric analysis. Dehydration products were analyzed by mass spectrometry and gas elution chromatography.

Results

Hydration of Isobutylene. Initially, shaker bomb hydration experiments, using pure isobutylene, were made with acidified IR-120 resin as catalyst at a water to isobutylene ratio of 1 to 1.

Table I. Batch Hydration of 2-Methylpropene with IR-120 Resin Catalyst

Only 2-methyl-2-propanol was produced

2-Methylpropene Content of Charge, Mole %	Conditions Temp., ° F.	Time, hr.	Resin/2-Methyl-propene Wt. Ratio	Max. Pressure, P.S.I.G.	Conversion to 2-Methyl-2-propanol, Mole %
100	210	3.2	0.65	325	69.5
72.6	200	3.5	0.85	325	54.0
18.8	200	3.5	0.95	400	24.0

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In these runs, conversions to *tert*-butyl alcohol as high as 69.5 mole % were obtained. Subsequent experiments, employing isobutylene of 72.6 and 18.8 mole % concentration, gave conversions to *tert*-butyl alcohol of 54 and 24 mole %, respectively. The remainder of the feed in these latter runs consisted of normal butenes and normal and isobutanes. No other product alcohols were detected (Table I).

Later experiments were made with pure isobutylene feed in a flow system to check the batch results, ascertain operability, and determine the effect of operating variables in mixed liquid-phase continuous processing.

In the first runs, concurrent upflow operation was attempted, but conversion to *tert*-butyl alcohol was extremely low. Concurrent downflow operation gave conversions to *tert*-butyl alcohol ranging from 64.5 to 70.9 mole % (average 67.5) at conditions of 200° F., 250 p.s.i.g., 1.0 hydrocarbon liquid hourly space velocity (LHSV, volume of hydrocarbon per hour per volume of catalyst), and a water to isobutylene ratio of 1 to 1. All subsequent experiments were made employing downflow operation.

Failure of the upflow operation is ascribed to the large mass transfer resistance at low liquid velocities in a flooded bed with a liquid system consisting of two almost completely immiscible phases. This results in poor water-hydrocarbon-catalyst contacting.

Table II. Analysis of Butane-Butene Stream

Compound	Concn., Wt. %
Propane	**2.03**
1-Propene	**0.52**
2-Methylpropane	**23.08**
1-Butane	**10.51**
2-Methylpropene	**22.57**
1-Butene	**14.23**
***cis*-2-Butene**	**9.10**
***trans*-2-Butene**	**16.22**
Butadiene	**0.27**
C_5 hydrocarbons	**1.01**
C_6 hydrocarbons	**0.45**

Table III. Batch Hydration of Pentenes with IR-120 Resin Catalyst Was Selective

Charge, Moles				Conditions			Conversion, Mole %	
2-Methyl-2-butene	2-Methyl-1-butene	1-Pentene	Water	Temp., ° F.	Time, hr.	Resin/olefin wt. ratio	To 2-methyl-2-butanol[a]	To 2-pentanol[b]
1.0	**0**	**0.95**	**4.5**	**200**	**55**	**1:1**	**12.6**	**1.7**
1.0	**1.0**	**0**	**4.5**	**200**	**22**	**1.05:1**	**29.5**	**. . .**

[a] Based on amylenes charged. [b] Based on 1-pentene charged.

Hydration of Refinery Butene-Butane Streams. Since a major source of isobutylene is catalytic cracker off-gas, process studies were made to determine conversions obtainable from C_4 refinery streams containing 18 to 23% (weight) isobutylene (Table II).

In this study, the effect of reaction temperature was investigated at selected conditions (Figure 1). As shown, a maximum conversion of 33.6 mole % was obtained at approximately 200° F. Conversions varied from 8.8 mole % at 252° F. to 19.2 mole % at 153° F.

Since equilibrium conditions are generally more favorable for alcohol formation the lower the reaction temperature, the conversions obtained at 153° to 155° F. are assumed to be rate limited. In contrast, at temperatures greater than 200° F., the reaction appeared to be equilibrium limited. This latter point was established in experiments at 200° F., 265 p.s.i.g., and 1.0 LHSV where *tert*-butyl alcohol in greater than the estimated equilibrium ratio of *tert*-butyl alcohol to isobutylene was added to the hydrocarbon-water feed. At lined-out conditions, the ratios of *tert*-butyl alcohol to isobutylene in the products were nearly equal to the ratios obtained in direct hydration experiments. These experiments established that at the higher temperatures (>200° F.) the reaction was indeed equilibrium, not rate, controlled. Further, at the higher temperatures, conversion to polymeric by-products was noted, confirming previous observations (*5*).

The effect of water to isobutylene mole ratio was studied in experiments employing mole ratios of 3 to 1, 4.7 to 1, 6 to 1, and 12 to 1 at selected conditions of 150° F., 160 p.s.i.g., and 1.0 hydrocarbon LHSV. Over this range, the water to isobutylene mole ratio had no appreciable effect on conversion in downflow operation. At the extreme mole ratios of 3 to 1 and 12 to 1, conversions obtained were 22.5 and 21.7 mole %, respectively. This study was made with an 18.8% (weight) isobutylene feed.

The effect of volume hourly space velocity was studied using space velocities of 1.0 to 6.0. Optimum conversion was obtained at a space velocity of about 4.0 (Figure 2). At this space velocity, conversion to *tert*-butyl alcohol was

Table IV. Analysis of C_5 Fraction from Debutanized Light Fluid Distillate

Compound	Concn., Wt. %
2-Methylbutane **3-Methyl-1-butene** ***cis*-2-Butene**	**18.32**
Pentane	**11.27**
1-Butene	**3.67**
2-Methyl-1-butene	**12.25**
2-Methyl-2-butene	**27.79**
2-Pentene	**21.21**
C_6 hydrocarbons	**5.56**

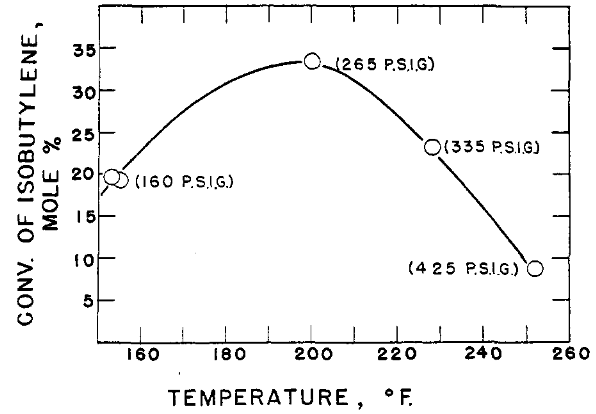

Figure 1. Maximum conversion, 33.6 mole %, occurred at 200° F.

Space velocity, 1.0 volume of hydrocarbon per hour per volume of catalyst; water to isobutylene mole ratio, 6 to 1; pressure, 25 p.s.i.g. greater than calculated saturation pressure; feed, butane-butene stream containing 18.8% (weight) isobutylene

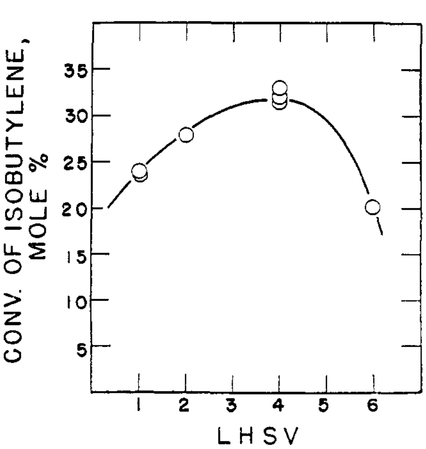

Figure 2. Optimum conversion was obtained when space velocity was about 4

Temperature, 200° F.; pressure, 265 p.s.i.g.; water to isobutylene mole ratio, 5 to 1; feed, butane-butene stream containing 22% (weight) isobutylene

Table V. Mixed Pentanols Can Be Selectively Dehydrated

Conditions		Alcohols Charged, Moles				Olefin Product Composition, Mole %						
Temp., ° F.	LHSV, vol./vol./ hr.	2-Methyl-2-butanol	2-Pentanol	1-Pentanol	Dehydrations Mole %	Butenes	3-Methyl-1-butene	2-Methyl-1-butene	2-Methyl-2-butene	1-Pentene	*trans*-2-Pentene	*cis*-2-Pentene
300	1	0.52	0.52	0.52	30.4	0.9	0	16.3	68.1	1.7	9.0	4.9
250	1	0.52	0.52	0.52	31.6	1.0	0.2	12.4	66.4	1.4	12.8	6.6
200	2.4	0.63	0.63	0.63	24.1	0.0	0.3	22.0	75.3	0.2	1.2	1.1
200	3.8	0.55	0.55	0.55	26.4	0.0	0.0	18.3	80.3	0.4	0.3	0.6

32.0 mole %; whereas, at space velocities of 2.0 and 6.0, the conversions were 28.0 and 20.2 mole %, respectively.

The unique increase in conversion with increasing space velocity in the 1 to 4 space velocity range can be attributed to better mixing of the two liquid phases, with a corresponding reduction in the large mass transfer resistance within the liquid phases at the higher liquid velocities in this range. The conversion at the space velocities in the 4 to 6 range appears to be dependent upon the chemical reaction rate and upon the diffusion rate in the porous resin spheres.

The data thus far reported were all obtained from runs of very low throughputs of 4 to 8 volumes of hydrocarbon per volume of catalyst. Therefore, to confirm the conversion at two temperature levels (200° and 157° F.) and determine catalyst life, a continuous experiment was made to a 360 volume throughput. The average conversion at 200° F. was 32 mole %, while the average conversion at 157° F. was 15 to 16 mole %. A second long throughput run employing a hydrocarbon feed containing 18.8% by weight isobutylene, at 200° F. and otherwise similar conditions, gave an average conversion of 27 mole % over a 320 volume throughput. In both runs, a negligible loss of activity was observed. This was in contrast to the results obtained in other experiments charging *n*-olefins at higher temperatures (300° to 350° F.) where rapid desulfonation of the ion exchange resin occurred, with a rapid loss of catalytic activity.

Hydration of Refinery C_5 Olefin Streams. Additional experiments were made to determine the possibility of selectively hydrating amylenes to *tert*-amyl alcohol in a similar manner (Table III). An initial batch experiment employing an equimolar mixture of isoamylenes (2-methyl-2-butene and 2-methyl-1-butene) gave a 29.5 mole % conversion to *tert*-amyl alcohol. Another experiment, employing an equimolar mixture of 2-methyl-2-butene and 1-pentene, showed that selective hydration was possible. Even at the long contact time employed (55 hours), only 1.7% of the 1-pentene was converted to *sec*-amyl alcohol (2-pentanol), while 12.6% of the 2-methyl-2-butene was converted to *tert*-amyl alcohol.

Subsequently, a long throughput flow experiment was made with a feed consisting of a typical C_5 olefin fraction from debutanized light fluid distillate (Table IV). This stream was processed downflow at a hydrocarbon liquid hourly space velocity of 1.0, 200° F., 150 p.s.i.g., and a water to amylene mole ratio of 2.9 to 1. The average conversion of the amylenes over a 112 volume throughput was 9.8 mole %, with no detectable catalyst aging. Also, in the flow experiments the formation of 2-pentanol was not detected, although the feed contained 21.2% 2-pentene. This high selectivity is attributed to the greater ease and rate of formation of the *tert*-amyl carbonium ion.

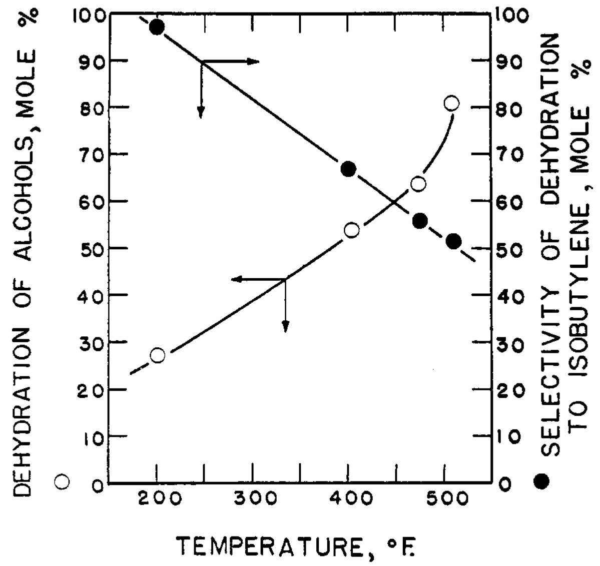

Figure 3. An equimolar mixture of *tert*-butyl(2 - methyl - 2-propanol) and *sec*-butyl(2 - butanol) alcohols was selectively dehydrated

Liquid hourly space velocity, 1.0; pressure, atmospheric

Selective Dehydration of Alcohols. Since selective hydration of olefins containing tertiary carbon atoms to tertiary alcohols was found possible, the possibility of effecting the reverse reaction selectively was briefly investigated. Initial experiments were made with an equimolar mixture of *sec*-butyl (2-butanol) and *tert*-butyl alcohols (Figure 3). At the proper conditions, selective dehydration of the *tert*-butyl alcohol can be obtained.

Additional experiments were made employing an equimolar mixture of *n*-amyl, *sec*-amyl, and *tert*-amyl alcohols (pentanols). These data (Table V) show that at properly selected conditions, an olefin product containing 98 to 99% of the desired methylbutenes can be obtained.

Based on these results, it is apparent that even if the hydration reaction were nonselective, subsequent selective dehydration of the product alcohols would enable the production of high purity branched olefins.

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