



CHAPTER 2

THEORY OF ISOPROPANOL SYNTHESIS

2.1 Literature Survey on Isopropanol Synthesis

2.1.1 Literature Survey on Propylene Manufacture (2)

Isopropanol could be synthesized in many ways from different raw materials in the presence of various catalysts and under different reactions.

In terms of raw material, it might be said that propylene was technically the most appropriate to manufacture isopropanol. S.B. Zdonik, E.J. Green, and L.P. Hallee (1974) prepared propylene for isopropanol synthesis by steam cracking. A mixture of hydrocarbon and steam was preheated to 870 K in the convective section of a pyrolysis furnace. Then it is further heated in the radiant section to as much as 1170 K. Steam reduced the hydrocarbon partial pressure in the reactor. The steam-to-hydrocarbon weight ratio was generally a function of the feedstock and ranged from 0.2 for ethane to greater than 2.0 for gas oil. In an olefins-plant separation train, propylene is obtained by distillation of a mixed C_3 stream containing propane, propylene and minor components, in a C_3 - splitter tower. Propylene is produced as the overhead distillation product, and the bottoms are a propane-rich stream. The size of the C_3 -splitter depends on the desired purity of the propylene product.

Propylene was obtained by R.B. Ewell and G. Gadmer from fluid catalytic cracking. A partially vaporized gas oil was contacted with zeolite catalyst. Contact time was 5 seconds-2 minutes and

pressure was 250 - 400 KPa (2.5 - 4 atm), depending on the design of the unit. Reaction temperature was 720 - 850 K. Converted feedstock formed gasoline-boiling-range hydrocarbons, C_4 and lighter gas, and coke. Propylene yield varied depending on reaction conditions, but yield of 2 - 5 % based on feedstock was common.

J.H. Gary and G.E. Handwork (1975) prepared propylene by thermal cracking process. Delayed coking and flexicoking or fluid coking, were used to convert residuum into more valuable products. In delayed coking, residuum and steam were heated in a furnace and then fed into an insulated drum where the free-radical decomposition of the feedstock took place. Coke eventually filled the drum and must be removed. In fluid coking, a residuum feed was injected into a reactor, where it was cracked thermally. Coke formed during the process deposited on other fluidized coke particles and was either removed by fluid coking or gasified by flexicoking. Both fluid and delayed coking occurred at 300 - 600 KPa (3-6 atm). Delayed coking was a lower temperature process (720 vs 820 K) and, thus, should have lower total olefin yields than fluid coking. H.G. Davis and R.G. Keister (1981) prepared propylene by advanced cracking techniques. Several groups are studying techniques to pyrolyze whole crude oil or various heavy petroleum fractions. These methods have in common very high temperatures, ultrashort residence times in the reactor zone, and rapid quench of the reaction products to minimize undesirable by-products. Among these techniques are the advanced cracking reactor from Union Carbide Corporation and thermal regenerative cracking from Gulf Oil, and Stone and Webster Engineering.

2.1.2 Literature Survey on Isopropanol Catalyst

As mentioned earlier, isopropanol may be synthesized in many ways from different raw material, in the presence of various catalysts and under different reactions. Faltings, Volkert; Knopf, Hans J; Liedmeier Franz; Riedel, Helmut (15) (1976) prepared isopropanol with up to 98 % selectivity by catalytic hydration of propylene at 125-155°C and 30-100 atm in the presence of a sulfonated cation exchange resin. The starting material moved downward through the reaction vessel, and the thickness of the catalyst bed was dependent on the velocity of the liquid phase: $D = (V - 70)/4.5$ where D = catalyst bed thickness and V = velocity of liquid phase in cm/hr.

Kuge, Masao; Yanai, Isamu (26) (1976) prepared alcohols by direct hydration of alkenes in the presence of H_3PO_4 absorbed in kieselguhr of large porous volume, which was suspended in high boiling organic solvents. Thus a porous H_3PO_4 catalyst prepared by mixing 4:1 wt. ratio of H_3PO_4 and kieselguhr and dried at 200°C was suspended in an organic solvent, through which was passed an equimolar mixture of propylene and steam at 170°C and 30 Kg/cm² gage to give isopropanol with 2.34 % conversion and 95.7 % selectivity compared to 2.28 and 95.7 % respectively with a conventional solid H_3PO_4 catalysts.

Chang, Clarence D; Morgan Norman J. (Mobil Oil Corp.) (8) (1980) studied hydration of C_{2-4} alkenes to alcohol catalyzed by zeolites. Thus 2-propanol was formed from propylene and water over HVSN-5 zeolite. No by-product diisopropyl ether was formed.

Sommer, August. Heitmann, Wilhem; Bruecker, Rainer (51) (1981) prepared hydration catalyst for C_{2-3} alkenes from montmorillonite clays (97 %), Group VI Oxides, and H_3PO_4 . The clay was treated with 20% HCl 82°C (8.4 mol HCl per Kg clay) and dried. Then WO_3 was

added to give 13 % WO_3 content, and the material treated twice with HCl, washed, dried, treated with 60 % H_3PO_4 and dried to give 35 % H_3PO_4 to give a catalyst for C_2H_4 hydration.

Schmidt Robert J.; Imai Tamotsu (46) (1981) hydrated olefins in H_2SO_4 containing cobalt sulfate (for corrosion minimization) at 100-300 °C and 1-250 atm to give alcohols. Propylene was hydrated at 201 °C and 65 atm to give isopropanol.

Mitsui Toatsu (36) (1981) reported that alcohols were prepared by hydration of olefins in the presence of H_3PO_4 and $GeO_2 \cdot 12WO_3 \cdot 30H_2O$ (I), and Cr compounds. Thus propylene was continuously supplied at 90 g/h to a mixture of 10 wt % H_3PO_4 and 1.5 wt % I, and chromium phosphate containing 10 ppm chromium in H_2O at 230 °C and 200 Kg/cm^2 gage to yield 11.4 wt % isopropanol. Similarly hydrated were C_2H_4 and $Me_2C : CH_2$.

Chemische Werke Huel A-G Ger offen (9) (1981) prepared catalysts for hydration of C_{2-3} alkenes to alcohols. The catalysts consisted of aluminosilicate (prepared from soluble Al and Si salts; wt ratio $Al_2O_3-SiO_2$ 1:5-7) calcined at 500-800 °C, treated with acid (e.g. HCl) to reduce the Al_2O_3 content to 1-5 (esp 1-3) wt %, surface area 280-380 m^2/g and, finally, treated conventionally with H_3PO_4 . Data for hydration runs with C_2H_4 and C_3H_6 were given.

Minachev, K.M., Mortikov, E.S.; Leontiev, A.S.; Smirnov, A.G.; Kononov, N.F.; Masloboev-Shvedov, A.A.; Zhomov, A.K; Kholdyskov, N.I. (35) (1976) prepared C_{2-5} alcohols from alkenes by treatment with H_2O at 150-280 °C and 30-70 atm in the presence of a catalyst comprising a type Y zeolite containing Ca^{2+} and > 1 of the following : Cr^{3+} , rare earth cation and Cr_2O_3 produced by calcining $Cr(OH)_3$. Thus, a mixture of H_2O and butenes (85% isobutene, 15% 1-butene and 2-butene) in a molar ratio 6:1 was contacted with a clay zeolite

containing Cr_2O_3 at 200°C and 60 atm with a space velocity of 1.5 hr^{-1} . The yield of C_4 alcohols (mainly Me_3COH) was 42-46 wt % and their composition in the product was 17-18 %.

Ciobanu Cornelia Serban, Gheorghe; Goidea, Dumitru; Georgescu, Adrian; Savu, Augenia; Gaber, Denu (Rafinarea "Vega" Plaiesti) (10) (1981) studied hydration catalysts comprising Mo, W, or P supported on diatomite with 15-20 % HCl at reflux. A P_2O_5 -diatomite catalyst was prepared and its activity for hydration of propylene at $190\text{-}200^\circ\text{C}$ was examined. Conversion to isopropanol was 2.56% after 3 hours and 2.05 % after 10 hours compared with 2.057 and 1.5 % respectively for a catalyst prepared by a known method.

Olah George Andrew (41) (1982) studied hydration of propylene to isopropanol on solid superacid catalysts based on perfluorinated sulfonic acids. Thus propylene was contacted with water and $\text{C}_{18}\text{F}_{23}\text{SO}_3\text{H}$ at 135°C , 700 psig to give isopropanol.

Slaugh, Lynn H.; Willis, Carl L (48) (1981) studied olefin hydration. Hydroxy sulfonic acids, prepared by the reaction of RCOR ($\text{R-R} = \text{H}$ or C_{1-7} hydroxaryl) with SO_2 and H_2O , were used as catalyst for the hydration of olefins to alcohols. Thus, $\text{HOCH}_2\text{SO}_3\text{H}$, prepared by treating aqueous HCHO with SO_2 , was used as a catalyst for the hydration of propylene to isopropanol (mol % yield 11.7) ; yield under similar conditions with $\text{P-MeC}_8\text{H}_4\text{SO}_3\text{H}$ and H_2SO_4 as catalysts were 3.8 and 4.6 mol %.

Mitui Toatsu Chemicals (1977) studied manufacturing of isopropanol by hydration of propene in the presence of aqueous H_3PO_4 under recycle. A Cr compound (80 ppm Cr) was added to the catalyst solution to prevent corrosion of ferrous reactors.

Bezman, Susan A. (3) (1982) investigated diisopropyl ether reversion in isopropanol production. Hydration of propene in the

presence of an acid ion exchange resin (e.g. Linde Silicate) gave a product mixture containing H_2O , isopropanol, diisopropyl ether, propene, propane, any C_4 hydrocarbons present in the feed, trace of alcohols or ethers derived from reaction of C_4 hydrocarbons and trace of C_6 hydrocarbon formed by dimerization of propene. This crude product mixture was passed through one or more conventional gas-liquid separation to separate propane, propene, and trace C_4 and lower hydrocarbons from the liquids, i.e. isopropanol, H_2O and diisopropyl ether. Diisopropyl ether was separated by column distillation and treated with a reversion catalyst (e.g. Amberlite XE 372) at 50 psig system and $330^\circ F$ to give propene and H_2O .

Imai, Tamotsu (20) (1980) synthesized alcohols from olefins. A.S. containing acid and a hydrophobic or hydrophilic carbon were used as catalysts for the hydration of C_{2-4} olefins to alcohols. Thus, an autoclave containing H_2SO_4 10.86 g, water 200.6 g, hydrophilic carbon 9.05 g, and a 35 : 36 propane-propene mixture 25.69 g was heated for 1 hour at $174^\circ C$ to give 51.1 % conversion of propene with 98.7 % selectivity to isopropanol. Without the carbon the conversion was 43.3% with 100% selectivity to isopropanol.

Chevron Research Co., Neth., (1983) prepared isopropanol for used as an antiknock agent from a propene feed by reaction with H_2O under hydrating conditions in a mixed phase in the presence of an acid-form cation exchanger catalyst, e.g. a sulfonated macrorectangular styrene-divinylbenzene copolymer. The conditions were $135-190^\circ C$, 6,900 -13,800 kPa, H_2O -propene mole ratio 1-15 and a propene space velocity of $0.15-1.5 \text{ hr}^{-1}$. Thus H_2O and propene rich feed from a catalytic cracker were passed through Amberlite XE 372 (83855-37-2) catalyst bed at $145^\circ C$ and 9930 kPa. The propene conversion was 69 % and the selectivity were isopropanol 90% and diisopropyl ether 10 %.

Bezman, Susan A. (4) (1983) manufactured isopropanol by treating a reactant stream containing H_2O and $(Me_2CH)_2O$ with a hydration catalyst, followed by reaction with propene in the presence of an acidic ion exchanger at 273-375 °F and 1,000-2,000 psig, and separating the liquid effluent into a product stream containing H_2O and Me_2CHOH and a recycle stream containing $(Me_2CH)_2O$. When the 2 reaction zones were maintained in the same reactor, the process might be conducted with a single catalyst e.g. Amberlite XE-372.

Braith Waite David G.; Pickle Joe D. (5) (1984) hydrated propylene over sulfonated ion exchangers at 130-150 °C, 250-350 psi to yield isopropanol. Thus propylene was treated with water in $EtO(CH_2CH_2O)_4Et$ containing Amberlyst 15 at 135 °C to give isopropanol.

Burton Paul E.; Wellman, William E. (6) (1982) studied indirect hydration of propylene to iso- Pr_2O and isopropanol which occurred by adsorption of propylene in 60-70% H_2SO_4 at 85-115 °C, 150-300 psig, withdrawal of a product containing 40-65 % H_2SO_4 and 10-40 % propylene, addition of 1.5-6 % (based on absorbed propylene) water, flashing the product at 100-800 °C, 5-10 psig to give an overhead containing products and aqueous H_2SO_4 containing depleted propylene. The bottom was recycled to the absorber, and the remainder was diluted with H_2O and heated to form more alcohols and ether. Tokuyama Soda Co., Ltd. prepared alcohols by hydration of olefins over heteropolyacid of $H_3PMo_{12}O_{40}$ containing Mn or V as soluble salts (0.1-10 g/l) in aqueous solution at 180-350 °C and pH 2-4.5. Thus propylene was heated with 0.6 g/l aqueous phosphovana domolybdic acid (0.1 N NaOH added to pH 3.3) at 240/200 Kg/cm^2 to give 10.9 wt % Me_2CHOH with 99% selectivity.

Kceal, Joseph A. (7) (1983) hydrated alkenes at 100-300 °C 10-500 psig over Zr-phosphate. Propylene was treated with water and Zr orthophosphate at 200 °C and 100 psig to give isopropanol.

Okumura, Yoshiharu; Kamiyama Setsuo; Furukawa, Hiroshi; Kaneko, Katsumi (Toa Nenryo Kogyo K.K.) (40) (1983) hydrated olefins to give alcohols using a solid catalyst-solvent system composed of either H-type mordenite or HY type zeolite with a silica-alumina (S-A) ratio of 20-500 and a sulfone solvent; or a H-type crystallization aluminosilicate with S-A = 20-500 and a solvent which is a C₂-C₆ oxyacid or lactone, lactide, or Me or Et ester. Thus HCl-washed H-mordenite containing 0.01 % Na₂O with an S-A of 108 catalyzed in 1-butene hydration in sulfolane-H₂O at 140 °C and 40 kg/cm² for 5 hours to give 15.7 % HOCHMeEt with 99 % selectivity.

Nieer, W. (38) (1984) discussed direct hydration of propylene to isopropanol. A review without references covered direct hydration of propylene with H₂O on sulfonated divinylbenzene-styrene copolymer to produce isopropanol.

Ono, Ryusuke; Sugirua, Tsutomu; Takemori Koje (Mitsui Toatsu Chemicals Co.Ltd) (42) (1972) prepared a catalyst for the hydration of olefins to alcohols by treating celite for 1 hr with boiling 10 % KOH, washing, then treating for another hr with boiling 10 % HCl, washing before drying and impregnation with aq.65 % H₃PO₄ to give the catalyst. H₂O-ethylene (mole ratio 6:1) was passed over the catalyst at 275 °C, 70 kg/cm², space velocity 2,000 l/hr to give 5.2 % C₂H₄ conversion into ethanol. Similarly, 2.1 % propylene and 2.9 % isobutene were converted into isopropanol and t-butanol, respectively.

Tabe, Kazo; Matsuzuke, Izumio (Mitsui Toatsu Chemicals Co., Ltd.) (52) (1972) prepared a TiO₂-ZnO catalyst for the hydration of olefins to alcohols. To be specific, NH₄OH was added to a solution of TiCl₄, (NH₄)₂SO₄, HCl and ZnCl₂ in H₂O and calcined for 3 hr at 400 °C to give the TiO₂-ZnO catalyst. ethylene-H₂O (1:1 mole ratio) was passed over the catalyst at 20 kg/cm², 265 °C and space velocity 3000

1/hr to give 2.76 % C_2H_4 conversion into ethanol. Similarly, 2.18 % propylene was converted into isopropanol.

Kanamuru, Muneaki, Ichikawa, Toshiyuki, Isumura, Ryuichiro; Ishii, Norimichi (Mitsui Toatsu Chemicals Co., Ltd.) (23) (1973) hydrated olefins to alcohols using a Re_2O_7 catalyst heating 86.1 g propylene with H_2O and 15 g 18.4 % aq. Re_2O_7 at $200^\circ C$ for 45 min in an autoclave gave 37.5 % isopropanol conversion and 91.2 % selectivity. Similar hydration of the olefins gave 9.1 % ethanol, 35 % t-butanol, 8.9 % sec-butanol, and 2.9 % 2-octanol.

Sommer, August; Urban, Martin (Veba Chemie A-G) (50) (1974) hydrated C_2H_4 to ethanol at $190-230^\circ C$ and 60-80 atm gauge, with a $H_2O-C_2H_4$ molar ratio of 0.1-0.3:1, whereas the hydration of C_3H_6 to isopropanol was carried out at $140-170^\circ C$ and 20-45 atm gauge with a $H_2O-C_3H_6$ molar ratio of 0.1-0.2:1. The catalyst in both cases was H_3PO_4 on acid-treated bentonite. Under these conditions the by-products, e.g., dimethylketone, ethyl ether were easily separated and could be recycled.

Rosscup, Robert J.; Zletz, Alex. Schaap, Luke A. (Standard Oil Co. (Indiana) (44) (1974) formed ethanol or isopropanol by catalytic hydration of the alkenes under high pressures over $Al_2O_3-SiO_2$. The alcohols were separated in a 2-phase H_2O -organic solvent extraction process aided by salting out the alcohols.

Saito, Yoshitaka; Okada, Yasuyoshi (Nippon Synthetic Alcohol Co., Ltd) (45) (1975) prepared catalysts for the hydration of olefins by adding at least 1 compound selected from alkali hydroxides, carbonates, and water-soluble silicates (0.3-10 wt. parts) to 100 wt. parts powdered silica gel or powdered silica gel-silicasol, blending, molding, calcination, and treatment with H_3PO_4 at $250-500^\circ C$, washing, drying and then impregnation with aq. H_3PO_4 solution. Thus, an aq.

solution containing 4 g NaOH was mixed with 250 g compound powdered silica gel. The mixture was blended, extruded molded, calcined for 3 hr at 680 ° C and then the solid catalysts was impregnated with 55 wt % aq. H_3PO_4 again to give a catalyst, over which (480 ml) were passed C_2H_4 and 0.5 molar equivalent H_2O at 60 kg/cm² gauge and 270 ° C to give ethanol with a single pass conversion of 5.1 mol %, compared to 4.1 mole % with a bentonite- Al_2O_3 catalyst. Similarly propylene was hydrated to isopropanol.

Matsuda Fujio ; Kato Takazo (Mitsui Toatsu Chemicals, Inc) (29) (1974) prepared alcohols by hydration of olefins in the presence of $(NH_4)_2SO_4$ or NH_4HSO_4 . Thus a mixture of propylene and $(NH_4)_2SO_4$ in H_2O was autoclaved for 1 hr at 230 ° C and 80 kg/cm² to give iso-propanol with 14.7 % conversion of propylene and more than 99 % selectivity for iso-propanol. Similarly, C_2H_4 and 1-butene were converted into ethanol and sec-butanol, respectively.

Matsuda, Fujio; Kato, Takazo (Mitsui Toatsu Chemicals Inc.) (30) (1976) hydrated olefins to alcohols in the presence of a strong acid ammonium salt (not NH_4 sulfate). Thus propylene was heated with 37.5 g/l.aq. NH_4Cl (pH 5.0) at 230 ° C and 180 kg/cm² for 1 hr in a stainless steel autoclave to give 10.2 % aq. isopropanol with 99 % selectivity. The catalyst caused no corrosion. Similarly ethylene or 1-butene was hydrated with NH_4NO_3 or NH_4Br as catalyst.

Zelinski, N.D. (Institute of Organic Chemistry) (54) (1974) treated C_{2-5} olefins with H_2O in the presence of an aluminosilicate catalyst, i.e., zeolite Y containing Ca and Cr and/or rare-earth-element ion and/or Cr_2O_3 at 150-280 ° C and 10-70 atm. Thus zeolite Y (Na form) and $Al(OH)_3$, were mixed, calcined at 550 ° C, impregnated with aq. solutions of $CaCl_2$ and rare-earth element (containing Ce 54.7, La 24.5, Nd 14.8 and Pr 44 %) next calcined, impregnated with

aq. Cr impregnated with aq. $\text{Cr}(\text{NO})_3 \cdot 9\text{H}_2\text{O}$ and dried at 200°C to give a catalyst. A mixture (1.6 molar ratio) of H_2O and butane-butene fraction (containing less than 40 % butene) was passed over this catalyst at 200°C and 50 atm to give 45-54 % butanols. Similarly prepared were isomyl alcohol, isopropanol and ethanol.

Ichikawa, Masaru (Sagami Chemical Research Center) (19) (1976) prepared polynaphthoquinone (I) catalyst, optionally its metal halide complex. I was prepared by the oxidation of naphthalenediol (1, 4-, 1, 7-, or 1, 5) with HNO_3 , or with air and H_2O_2 (in alcohol or FeCl_3 (in H_2O) as catalysts at 70°C and treated with a transition metal halide (II) in a sealed tube or in alcohol to give I-II complex. Propylene was mixed with 3 vols of nitrogen, saturated with H_2O , and passed over 9:1 I- FeCl_3 at 300°C to give a liquid containing isopropanol 93 % and dimethylketone 7 %, with 12.2 % conversion of propylene. Similarly, ethylene gave ethanol, butene gave sec-butanol and isobutene gave ter-butanol.

Matsuda, Fujio, Kato, Takazo (Mitsui Toatsu Chemicals Inc.) (31) (1976) hydrated olefins to alcohols by treating with water in the presence of Be salts. Thus 37.5 g/l RCH:CH_2 (R = H, methyl or ethyl) were treated with water at 300°C and 250 kg/cm^2 for 3 hr in the presence of BeSO_4 , BeCl_2 , or $\text{Be}(\text{NO}_3)_2$ at pH = 3 to give 97-99 % ethanol, isopropanol and sec-butanol, respectively.

Matsuda, Fujio; Kato, Takazo (Mitsui Toatsu Chemicals, Inc.) (1975) hydrated olefins in the vapor phase in the presence of Be salts, alkali metal acid sulfates or alkali metal silicotungstates. Thus, SiO_2 was impregnated with 25 wt % aq. BeSO_4 dried for 1 hr at 180°C and a mixture of propylene and H_2O was passed at 180°C to give an aq. solution containing 21.4 wt % isopropanol. Analogously, ethylene and butylene were converted into ethanol and sec-butanol, respectively.

Rosak, Josef; Novotny, Bohumil; Chlouba, Vaclav, Koppecky, Ivan, Kubicka, Rudolf (43) (1978) studied the reaction mixture from the hydration of olefin yielding monohydric alcohols in a vertical multiplicate column. The reaction mixture was neutralized with aq. NaOH and condensed in 2 steps yielding, respectively, (a) a part of the water content with dissolved H_3PO_4 and the bulk of inorganic salts and (b) residual aq. product, which was rectified to yield the alcohol ethanol, propanol, and demineralized water, which was recycled to the hydration process. The process saves demineralized water and prevents contamination of the final product and applies with entrained H_3PO_4 and catalyst.

Matsuda, Fujio; Kato, Kazo (Mitsui Toatsu Chemicals, Inc.) (33) (1979) hydrated olefins in the liquid phase by reaction with H_2O in the presence of Mg salts. Thus a mixture of 20-60 ml propylene, 4.8 g $MgSO_4$ and 80 g H_2O was autoclaved for 1 hr at 250° C and 150 kg/cm² nitrogen to give ethanol (13.4 % in the product mixture) with 99 % selectivity. No corrosion of the reaction vessel was observed. Similarly, ethylene and butylene were converted to ethanol and 2-butanol, respectively. $MgCl_2$ and $Mg(NO_3)_2$ were also used.

Tsybuljevskii, A.M.; Novikova, L.A.; Kondrat'ev, V.A.; Tolkacheva, L.N., Mortikov, E.S.; Breschenko, E.M.; Minachev, Kh.M. (53) (1979) studied zeolites containing Ca^{2+} , Ni^{2+} , Cr^{3+} , and rare earth cations as catalysts for the hydration of C_2H_4 (I), propylene (II), and iso-butylene at 200-350° C and 7-14 MPa using olefin- H_2O at molar ratio 1:1-10. The H-exchanged zeolite containing Cr^{3+} gave the best result, hydrating I and II with 9.6 % and 17.8 % conversion, respectively 100 % selectivity and useful life of 380 hr. The activity of this catalyst increased sharply with the pressure.

Sommer, August; Bruecker, Rainer (chemische Werke Huels A.-G.) (51) (1980) prepared montmorillonite-supported H_3PO_4 catalyst and used it for the hydration of C_2 - C_3 alkenes to alcohols. Thus, 110 g/h ethanol and 300 g/h isopropanol were obtained using the catalyst.

Gross Stephen E. (16) (1981) mixed natural diatomite 8-12 %, bentonite clay 4-6 %, SiO_2 4-6 %) cellulose fiber 1.5-2.5 %, corn meal 1.5-2.5 %, and H_2O , then extruded, pelleted, dried, and calcined it to form porous catalyst support pellets. The dried pellets were calcined at a temperature of over $1200^\circ F$ for more than 30 min until the corn meal and cellulose fibers were completely removed from the pellets, leaving a highly porous solid composite pellet of natural diatomite, bentonite clay, and SiO_2 . The drying was conducted at 180 - $400^\circ F$ for 25-35 min, Suitable calcining temperature were 1200 - $1300^\circ F$, for times of 40-50 min. The application of such supports impregnated with H_3PO_4 in the catalytic conversion of ethylene to ethanol was indicated. The supports contained 45-55 wt % natural diatomite, 20-30 wt % bentonite clay, and 20-30 wt % SiO_2 .

Maruzen Oil Co., Ltd. (28) (1982) studied hydration of olefins to give alcohols. $xMnO : Al_2O_3 : ySiO_2 : zH_2O$ ($x = 0.9 \pm 0.2$, $M = \text{cation}$, $m = 1, 2$; $y = 5-300$; $z = 0-40$) were used as catalysts. Thus, aluminosilicate (ZSM-5), $0.35 (Pr_4N)_2O : 0.71 Na_2O : Al_2O_3 : 48.8 SiO_2$ was prepared and treated with 5N-HCl and calcined at $600^\circ C$ to give a catalyst. Propylene and H_2O were autoclaved for 2 hr. at $200^\circ C$ to give a product containing 9.5 wt % isopropanol.

Cals. Rolf Rainer; Osterburg, Guenther; Prezelz, Mildn, Webers, Werner (Deutsche Texaco A-G) (7) (November, 1987) prepared $i-C_3H_7OH$ at $120 - 200^\circ C$, 60 - 200 bar by injecting a propene containing C_3 hydrocarbon stream into one end and processed water (1-50 mol/mol propene) into the other end of a series of 2-10 reactors which

contained strongly acid cation exchange resins and are connected in such way that the hydrocarbon stream and the water traveled in the countercurrent fashion through the series of reactors. The process was found to give high conversion (e.g., 99.6 %) of propene with high selectivity (e.g. 99.4 %) to isopropanol

Okumura, Yoshiharu; Kamiyama, Setsuo; Furukawa, Hiroshi; Kaneko, Katsumi (Toa Nenryo Kogyo K.K) (40) (1984) hydrated olefins to make alcohols by using a solid catalyst-solvent system composed of either H-type mordenite or HY zeolite with a silica-alumina (S-A) ratio of 20-500 : 1 and a sulfone solvent; or a H-type crystalline aluminosilicate with S-A = 20-500 : 1 and a solvent which is a C₂-C₅ oxy acid or lactone, lactide, or Me or Et ester thereof. For example, HCl-washed H-mordenite containing 0.01 % Na₂O with an S-A of 108 : 1, catalyzed 1-butene hydration in sulfolane - H₂O at 140 °C and 40 kg/cm² for 5 hour to give 15.7 % HOCHMeEt with 99% selectivity.

Equchi, Koichi; Tokiai, Takeo; Kimaru, Yoshio; Arai, Hiromichi (Grad. Sch. Eng. Sci., Kyusho University, Fukuoka, Japan 816) (13) (1986) prepared high-pressure catalyst to hydrate olefins over various proton exchanged zeolites. Catalytic hydration of C₂H₄, C₃H₆ and 1-butene to their respective alcs. was investigated at high pressure using proton - exchanged zeolite. All the zeolites exhibited hydration activities. Pentasil and ferrierite-type zeolites were the most active among the zeolite catalysts tested. The activities of the zeolites were successfully correlated with the amount of adsorbed water, indicating that hydrophobic acid sites were effective for olefin hydration.

Sekizawa, Kazuhiko, Hironaka, Toshio; Fujii, Satoshi; Tsutsumi, Yukihiro (Toyo Soda Mfg. Co., Ltd.) (47) (1985) prepared alcohols by hydration of olefins in the presence of a catalyst which

was prepared by calcination of ferrierite at 400-900 °C in the presence of steam. For example, passing isobutene/water (1 : 1) over the catalyst (GHSV 750 hr⁻¹), prepared by calcination of ferrierite at 800 °C in the presence of 30 °C steam, gave ter-butanol with 99.7 % selectivity.

Kikuchi, E.; Matsuda, T.; Shimomura, K.; Kawahara, K.; Morita, Y. (Sch. Sci. Eng., Waseda University, Tokyo, Japan 160). (25) (1986) studied the hydration of ethene, propene, 1-butene, and isobutene on protonic zeolite catalysts. The catalyst was investigated at atmospheric pressure in a continuous flow system. Highly siliceous zeolites, such as ferrierite and ZSM-5 were found to be very active, and mordenite moderately active for ethene hydration, while hydrophilic Y and L zeolite were inactive. In particular, the ferrierite having a SiO₂/Al₂O₃ ratio of 17 : 1 was the most active on a per gram of catalyst basis. When propene or 1-butene was hydrated instead of ethene, the activity of the ferrierite became smaller than that of ZSM-5. Furthermore the activity of ferrierite for isobutene hydration was smaller than that of mordenite. These results were attributed to the shape-selective effect exhibited by ferrierite having small pores.

Ballantine, James Archibald; Diddams, Paul Arther; Jones, William; Pernell, John Howard; Thomas, John Meuring (British Petroleum Co. PLC) (2) (1987) reported that layered clays, in which the interlamellar charge (defined by the clay cation exchange capacity) was sufficient only to permit expansion of the sheets to accommodate a single liquid layer, are used as catalysts in reactions capable of catalysis by protons. The catalysts are prepared by cation-exchanging the clay using a solution comprising a source of either alkali metal or alkali earth metal cations, then heating the cation-exchanged clay at 200-500 °C to produce a single liquid layer in the interlamellar region of

the clay. For example, a 1 % suspension of Gel-White L (montmorillonite having a reduced cation exchange capacity (CEC) 101 ± 8 mequiv./100 g) was stirred at room temp. for 6 hour in 1 N ag. solution of the chloride salt of the exchanging cation, the supernatant liquid discarded and the process repeated, after which the exchanged clay was washed with H_2O and centrifuged repeatedly until no Cl^- was detected in the washings. Coionic Na^+ and Li^+ exchanged clays were heated at $200^\circ C$ for 24 hour, and then the Na^+ was removed by cation exchange with Al^{3+} . A reactor was charged with 0.3 g of this catalyst (CEC 46 mequiv./100 g), 2.05 ml 1-hexene and 0.95 mL AcOH. After 4 hour at $160^\circ C$, the product contained 34.5 mole % of a mixture of 2-hexyl acetate (I) 3-hexyl acetate (II) and hexene isomers (III), with relative selectivities for I 26.5, II 10.8, and III 62.8 % respectively.

2.2 Basic Knowledge of Isopropanol

Isopropanol (2-propanol, dimethylcarbinol, sec-propanol) is the lowest member of the class of secondary alcohols. As one of the lower ($C_1 - C_5$) alcohol, isopropanol is second in commercial production to methanol. U.S. production of isopropanol in 1978 was 7.9×10^5 metric tons. Changing technology has also influenced the relative production of these alcohols in recent years, e.g., loss of isopropanol production for acetone is somewhat less influential than that of ethyl alcohol for use in the acetaldehyde-based manufacture of n-butanol and 2 - ethyl - 1 - hexanol. In terms of physical properties, isopropanol is a colorless, volatile, flammable liquid. Its odor is slight, resembling a mixture of ethanol and acetone. It has a bitter, unpotable taste. The physical and chemical properties of isopropanol reflect its secondary hydroxyl functionality. For

example, its boiling and flash points are lower than n-propanol, whereas its vapor pressure and freezing point are significantly higher. Thus, isopropanol boils at only 4°C higher than ethanol and possesses similar solubility properties, which accounts for the competition between these two products in many solvent applications. Three grades of isopropanol, which differ mainly in water content are marketed in the United States : anhydrous, 95 vol % and 91 vol %, which is an azeotrope (with water) and usually is referred to as CBM (constant-boiling-mixture) isopropanol.

In terms of chemical properties, most of isopropanol chemistry involves the introduction of the isopropyl or isopropoxy group into other organic molecules. The use of isopropanol for this purpose accounts for 60 % of its production. Much of the production is for the manufacture of agricultural chemicals, pharmaceuticals, process catalysts, and vents.

2.2.1 Uses of Isopropanol

Isopropanol is used as chemicals, solvents, and medicals. Estimated U.S. uses in 1977 were acetone, 38 %; other chemicals, 7 %; coatings and other solvents, 30 %; drugs and cosmetics, 10 %; miscellaneous, 8 %; and export, 7 %.

Chemicals Growth of the use of isopropanol as a feedstock for the production of acetone will be influenced by alternative routes to, and markets for, the production of acetone. In addition, isopropanol is consumed in the production of other chemicals.

Table 2.1 Spectral Specifications for Isopropyl Alcohol

Property	ACS reagent 1975	1980 USP XX and NF XV	ASTM D 770-80	Federal TT-1-735, grade A	ASTM D 1310-81, 91 vol % IPA
acidity, wt %					
acetic acid, max	0.0008	0.0024	0.002	0.002	
alkalinity, wt %					
NaOH, max	0.0005				
appearance				CFSM ^a	
color (Pt-Co), max	10	colorless	10	10	
corrosion on copper				no pitting or black stain	
distillation, initial bp,					
min-dry point, max, °C				81.3-83.0	
range, °C, max	1.0 (must include 82.3°C)		1.5 (must include 82.3°C)		1.0 (must include 80.4°C)
nonvolatile matter, g/100 mL, max	0.0008	0.005	0.005	0.002	
odor					
initial			characteristic	characteristic	
residual			none	none	
refractive index, n_D^{20}		1.376-1.378	0.785-0.787	0.7862-0.7870	0.8175-0.8185
sp gr (20/20°C)	0.7883	0.783-0.787 ^b			
uv spectrum	smooth curve ^c				
max absorbance					
at 210 nm	1.00				
220	0.40				
230	0.20				
245	0.08				
260	0.04				
275	0.03				
300	0.02				
330	0.01				
water content, wt %					
max	0.2		0.2	0.10	
water solubility	clear		no turbidity	no turbidity	

^a Clear and free of suspended matter.

^b At 25°C.

^c For spectrometric grade only.

Solvents Because of the balance between alcohol, water, and hydrocarbonlike characteristics, isopropanol is an excellent low cost solvent which is free from the government regulations and taxes that

Table 2.1 Special Specifications for Isopropyl Alcohol

Property	ACS reagent 1975	1980 USP XX and NF XV	ASTM D 770-80	Federal TT-1-735, grade A	ASTM D 1310-81, 91 vol % IPA
acidity, wt %					
acetic acid, max	0.0008	0.0024	0.002	0.002	
alkalinity, wt %					
NaOH, max	0.0005				
appearance				CFSM ^a	
color (Pt-Co), max	10	colorless	10	10	
corrosion on copper				no pitting or black stain	
distillation, initial bp,					
min-dry point, max, °C				81.3-83.0	
range, °C, max	1.0 (must include 82.3°C)		1.5 (must include 82.3°C)		1.0 (must include 80.4°C)
nonvolatile matter, g/100 mL, max	0.0008	0.005	0.005	0.002	
odor					
initial			characteristic	characteristic	
residual			none	none	
refractive index, n_D^{20}		1.376-1.378	0.785-0.787	0.7862-0.7870	0.8175-0.8185
sp gr (20/20°C)	0.7883	0.783-0.787 ^b			
uv spectrum	smooth curve ^c				
max absorbance					
at 210 nm	1.00				
220	0.40				
230	0.20				
245	0.08				
260	0.04				
275	0.03				
300	0.02				
330	0.01				
water content, wt %					
max	0.2		0.2	0.10	
water solubility	clear		no turbidity	no turbidity	

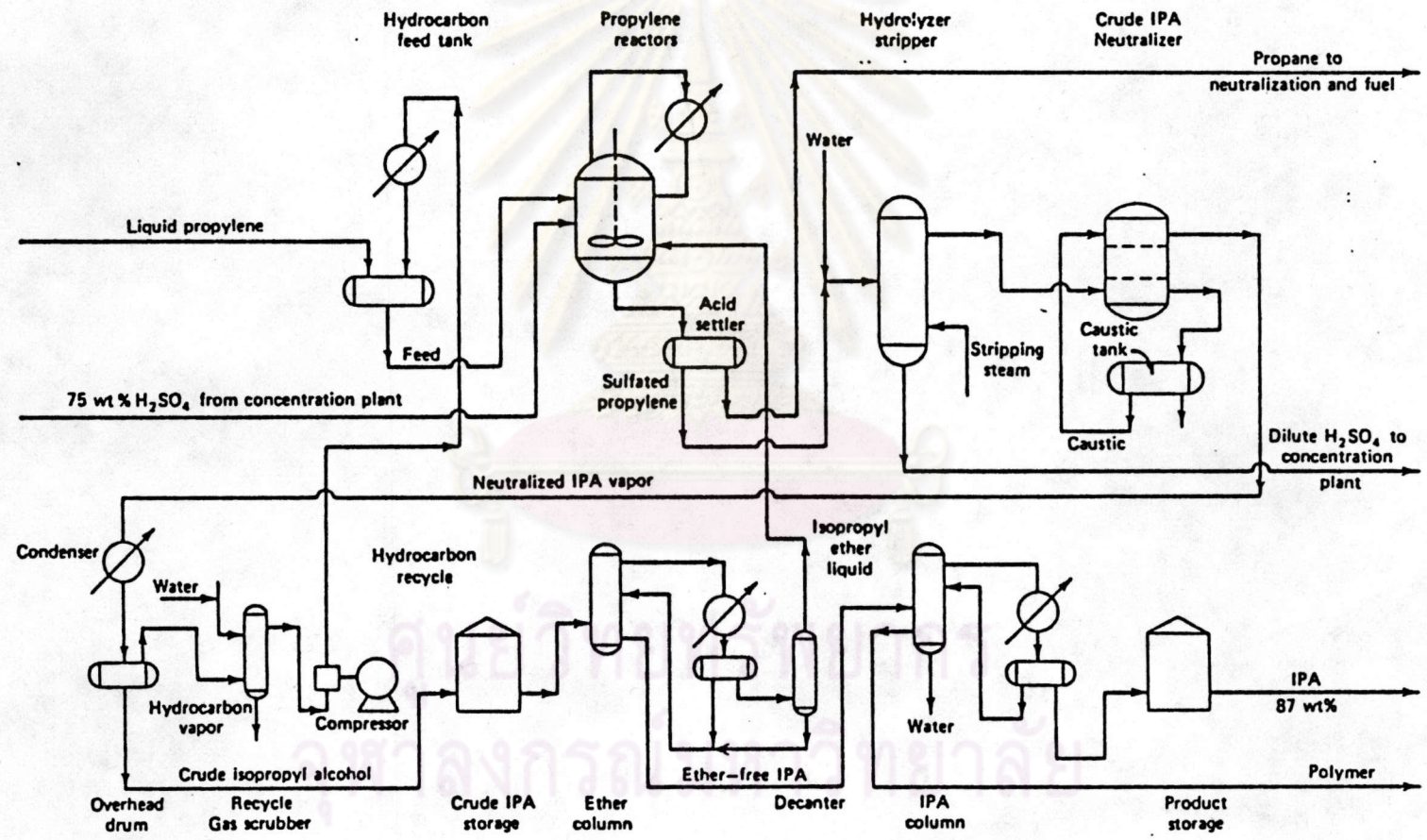
^a Clear and free of suspended matter.

^b At 25°C.

^c For spectrometric grade only.

Solvents Because of the balance between alcohol, water, and hydrocarbonlike characteristics, isopropanol is an excellent low cost solvent which is free from the government regulations and taxes that

Figure 2.1 Indirect Hydration for Manufacture of isopropyl alcohol, Courtesy of Gulf Publishing Company



apply to ethanol. The lower toxicity of isopropanol favors its use over methanol, even though the former is somewhat higher in cost. Consequently, isopropanol is used as a solvent in many consumer products as well as industrial products, and processes e.g. gasification and extractions. It is a good solvent for a variety of oils, gums, waxes, resins, and alkaloids and, consequently, it is used for preparing cements, primers, varnishes, paints, printing inks, etc.

Isopropanol is also employed widely as a solvent for cosmetics, lotions, perfumes, shampoos, skin cleansers, nail polishes, make-up removers, deodorants, body oils, and skin lotions. In cosmetic applications the acetone-like odor of isopropanol is masked by the addition of fragrance.

Over 68 aerosol products containing isopropanol solvent have been reported. Aerosol formulations include hair sprays, floor detergents, shoe polishes, insecticides, burn ointments, window cleaners, waxes and polishes, paints, automotive products, e.g. windshield deicer, insect repellents, flea and tick spray, air refreshers, disinfectants, veterinary wound and pinkeye spray, first-aid spray, foot fungicide, and fabric wrinkle remover.

Medicals Isopropanol also is used as an antiseptic and disinfectant for home, hospital, and industry. It is about twice as effective as ethanol in these applications. Rubbing alcohol, a popular 70 vol % isopropanol-in-water mixture, exemplifies its medicinal use. Other examples include 30 vol % isopropanol solutions for medicinal liniments, tinctures of green soap, scalp tonics and tincture of mercuraphen. It is contained in pharmaceuticals, e.g. local anesthetics, tincture of iodine, and bathing solutions for surgical sutures and dressings. Over 200 uses of isopropanol have been tabulated.

2.2.2 Manufacture of Isopropanol

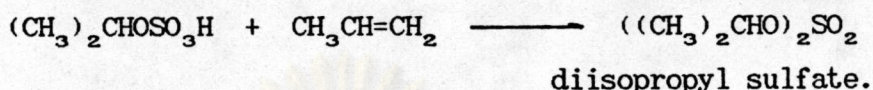
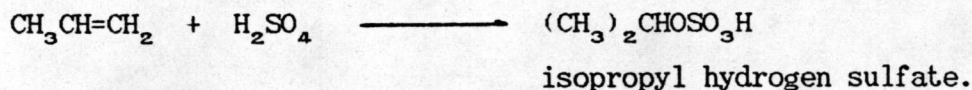
There are two basic processes for the commercial manufacture of isopropanol, and each involves synthesis from propylene. The standard method since 1920 is the indirect - hydration process (esterification-hydrolysis or the sulfuric acid method), which involves reaction of propylene with sulfuric acid. Although indirect hydration is the only process used in the United States, it is being replaced rapidly in Europe and Japan by newer processes involving catalytic hydration of propylene, i.e, direct hydration with the use of superheated steam and high pressures. High corrosion, high energy costs, and air pollution by the indirect process has led to alternative processes in Europe. However, high purity propylene feedstock is not required in the indirect hydration process. Thus a C_3 -feedstock stream from refinery-off gases containing 40-60 wt % propylene is used in the United States.

Other potential synthetic methods include fermentation of certain carbohydrates, oxidation of propane, hydrogenation of acetone, and hydrolysis of isopropyl acetate. None of these methods are practiced commercially.

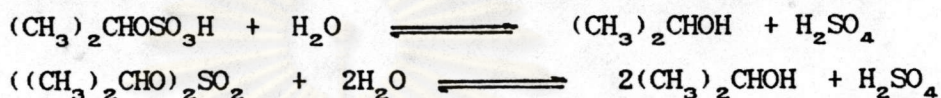
1. Indirect Hydration

Indirect hydration is based on a two-step reaction of propylene with sulfuric acid. In the first step, mixed sulfate esters, primarily isopropyl hydrogen sulfate are formed. They are then hydrolyzed, forming the alcohol and sulfuric acid.

Step 1. Formation of mono- and di-isopropyl sulfates.

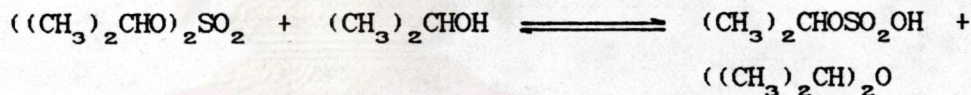


Step 2. Hydrolysis of the sulfates to isopropyl alcohol

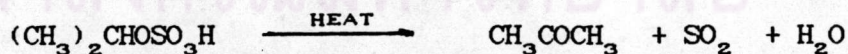


By-Product

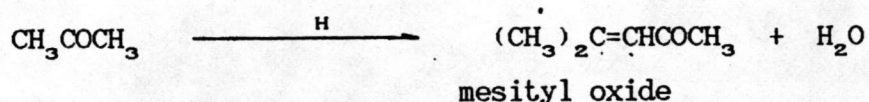
Diisopropyl ether is the principal by-product formed by reaction of the intermediate sulfate esters with isopropanol.



Other significant by-products include polymers, acetone, propionaldehyde, hydrocarbons, and carbonaceous material. Many by-products arise from acid-catalyzed polymerization and oxidation of propylene or isopropanol. Minor contaminants arise from impurities in the feed. Acetone, an oxidation product, also forms from thermal decomposition of the intermediate sulfate ester, e.g.



In addition to generating malodorous sulfur dioxide, the acetone formed can undergo further condensation in the acidic medium to generate mesityl oxide and higher products.



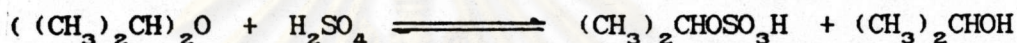
High propylene concentrations in the presence of acids can form dimers, trimers and higher homologous, which can polymerize or hydrate to C_8 , C_9 and higher alcohols, and olefins. These derivatives can emit musty, woody, and camphoraceous odors, and their reaction products with sulfur - containing compounds can give a catalyst odor to the product. Odor can be improved by employing appropriate reaction conditions and by contacting isopropanol with various metals, e.g., copper and nickel, or certain partially reduced metal oxides.

Process A typical indirect-hydration process is presented schematically in Figure 2.1.

In the process, crude liquid propylene reacts with sulfuric acid (>60 wt %) in an agitated reactor at moderate pressure (2.2 - 2.9 MPa (300-400 psig)). The isopropyl sulfate esters form and are maintained in the liquid state at 20 - 70° C. Low propylene concentrations, i.e., 50 wt %, can be tolerated, but concentrations of 65 wt % or higher are preferred to achieve high alcohol yields. Since the reaction is exothermic, cooling helps minimize corrosion.

There are two general operational modes practiced for conducting the reaction. In the two-step strong-acid process, separate reactors are used for the propylene adsorption and sulfate ester hydrolysis stages. The reaction occurs at high sulfuric acid concentration (> 80 wt %) and at 1-1.2 MPa (130-160 psig) and low temperature, e.g., 20-30° C. The weak acid process is conducted in a single stage at low acid concentration (60-80 wt %) and at higher pressure and temperature, i.e., 2.5 MPa (350 psig) and 60-65° C, respectively. Isopropanol selectivities in excess of 90 % are obtained from both acid processes.

The sulfate ester hydrolysate is separated in a stripper to give a mixture of isopropanol, isopropyl ether, and water overhead and dilute sulfuric acid bottoms. The overhead is neutralized in a scrubbing tower containing sodium hydroxide and is refined in a two-column distillation system. Diisopropyl ether is taken overhead in the first, i.e. ether, column. This stream is generally recycled to the reactors to produce additional isopropanol by the following equilibrium reaction:



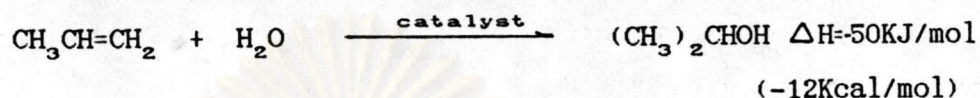
Wet isopropanol (87 wt %, 91 vol %) is taken overhead in the second still. More than 93 wt % of the charged propylene is converted to isopropanol in this system.

The 91 vol % alcohol is sold as such or is dehydrated by extractive distillation with diisopropyl ether or cyclohexane to produce an anhydrous product. The wet isopropanol is fed at about the center of a dehydration column, and the azeotroping agent is fed near the top. As the ternary azeotrope forms, it is taken overhead, condensed, and the layers are separated. The upper layer, which is mainly azeotroping agent and alcohol, is returned to the top of the column as reflux. The lower layer is mostly water. Anhydrous isopropanol is removed from the base of column.

Manufacturing plants in the United States are believed to use solely indirect propylene hydration. Several European companies, e.g., British Petroleum, Shell, and Deutsche Texaco, also employ this older technology in plants in Europe and Japan.

2. Direct Hydration

The acid-catalyzed direct hydration of propylene is exothermic and resembles the preparation of ethanol from ethylene.



The equilibrium can be controlled to favor product alcohol if high pressures and low temperatures are applied. However, the advantage of low temperature cannot be utilized, because all known catalysts require moderate temperatures to be effective.

There are three basic processes in commercial operation.

(1) Vapor-phase hydration over a fixed-bed catalyst of supported phosphoric acid (Veba-Chemie), or silica-supported tungsten oxide with zinc oxide promoter. (ICI) (3)

(2) Mixed vapor-liquid phase hydration at low temperature (150° C) and high pressure (10.13 MPa (100 atm)) with a strongly acidic cation-exchange resin catalyst. (Deutsche Texaco AG) (4)

(3) Liquid-phase hydration at high temperature and high pressure (270° C, 20.3 MPa (200 atm)) in the presence of a soluble tungsten catalyst (Tokuyama Soda).

A typical process scheme for direct hydration of propylene is shown in Figure 2.2.

The manufacture of isopropanol by the direct catalytic hydration of propylene was begun in 1951 by ICI. The plant used a WO_3 -ZnO catalyst supported on SiO_2 , high temperature (230-290° C), and high pressure (20.3-25.3 MPa (200-250 atm))

In the Veba-Chemie process (see Fig. 2.2) a vaporized stream of propylene and water is passed through an acidic catalyst bed (H_3PO_4

supported on SiO_2) at 240–260 °C and 2.5–6.6 MPa (25–65 atm) The gas stream from the reactor is cooled and fed to a scrubber where the remaining isopropanol is removed. Isopropanol selectivity is 96 % for the gas phase process. Owing to equilibrium limitations in the gas phase at high temperature and low pressure, a low propylene conversion (5–6 %) results and, thus, a large amount of unreacted propylene is recycled. Both of the above processes involve high plant costs owing to high pressure requirements, gas recycles, and the requirement for high purity propylene (99 %).

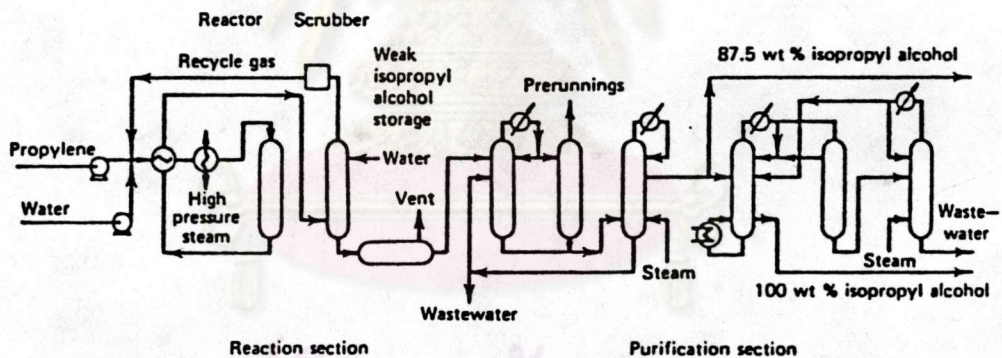
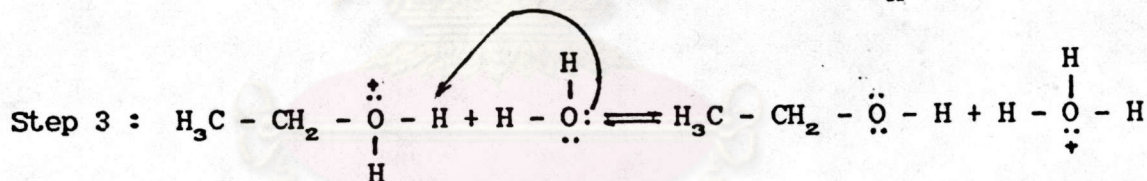
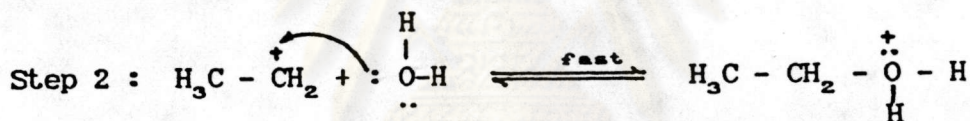
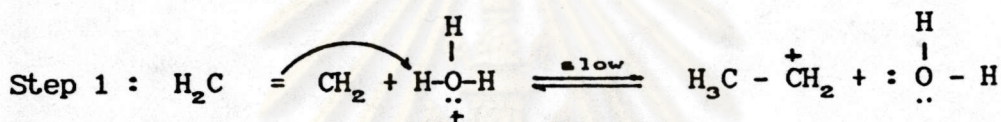


Figure 2.2 Veba-Chemie's direct hydration for manufacture of isopropyl alcohol. Courtesy of Gulf Publishing Company.

2.3 Hydration Mechanism of Alkenes

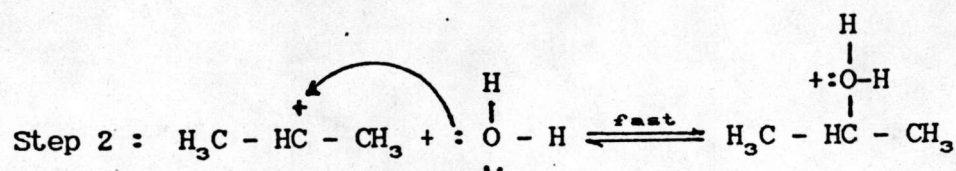
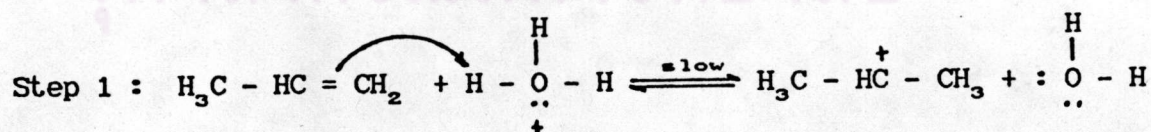
The acid-catalyzed addition of water to the double bond of an alkene (hydration of an alkene) is a method for the preparation of the corresponding low-molecular-weight alcohol, which finds its greatest utility in a large-scale industrial process. The addition of water to the double bond follows Markovnikov's rule. In general the reaction takes the form as follows.

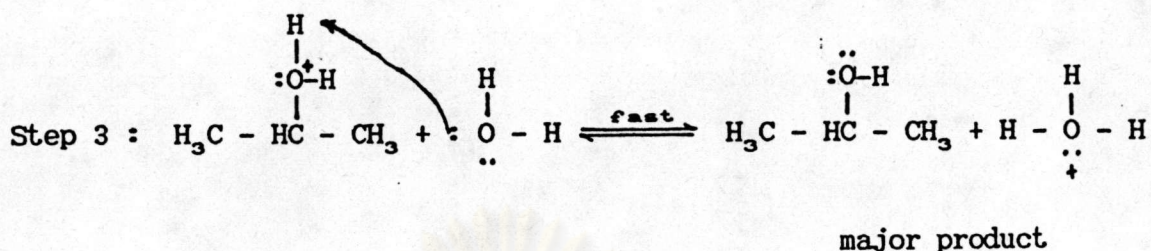
Hydration of ethene to ethanol :



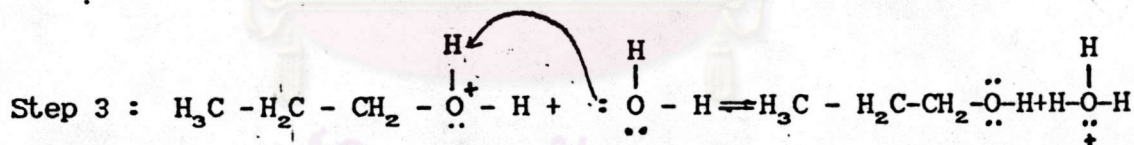
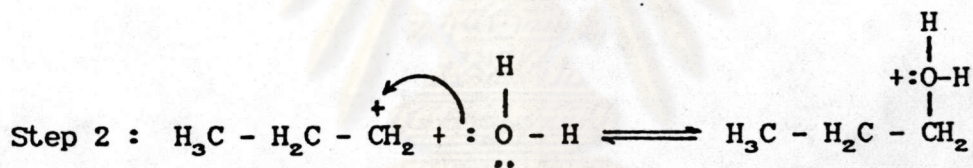
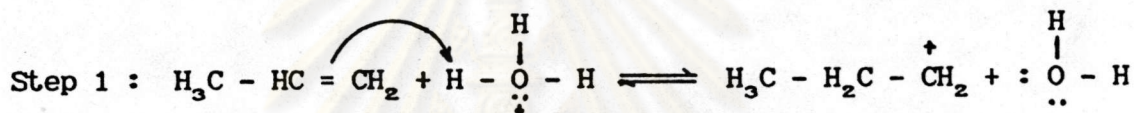
Since the reactions follow Markovnikov's rule, the acid-catalyzed hydration of an alkene does not yield primary alcohol, except in the case of the hydration of ethene.

Hydration of propene to isopropanol





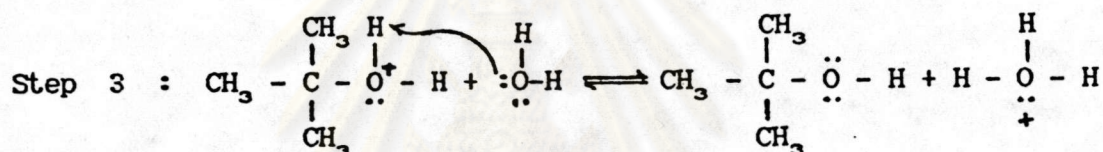
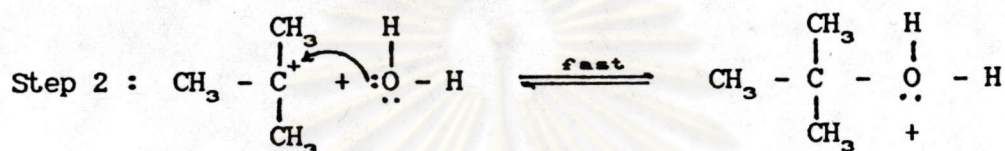
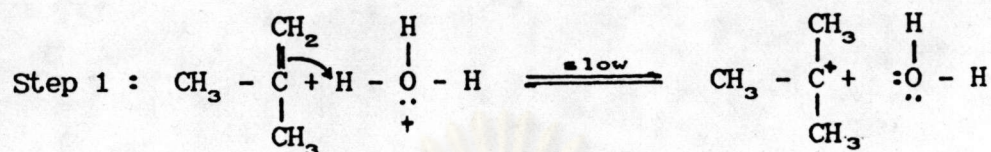
In addition, n-propanol (minor product) occurred along with isopropanol (major product), as follows:



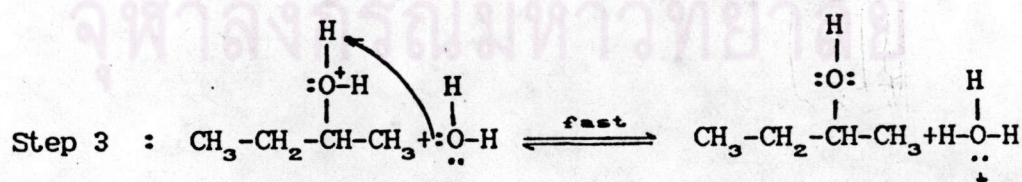
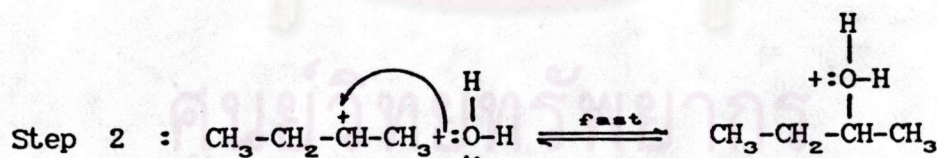
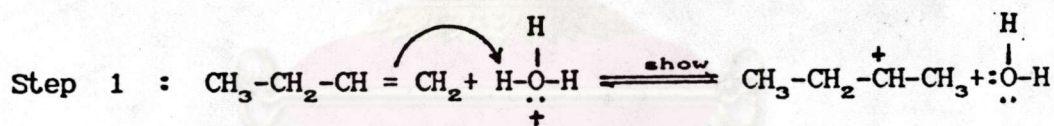
minor product

The rate limiting step in the hydration mechanism is step 1, the formation of the carbocation. It is also this step that accounts for the Markovnikov addition of water to the double bond. Similarly, the hydration mechanism for C_4 -alkenes is:

Hydration of iso-butene to ter-butanol:

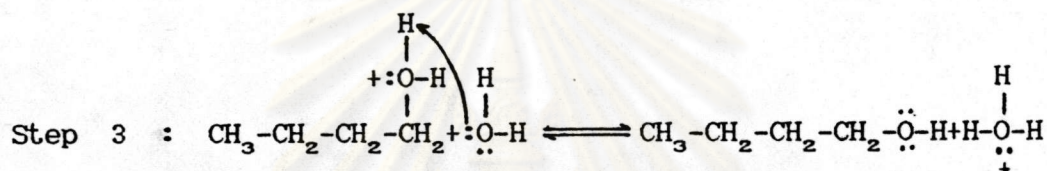
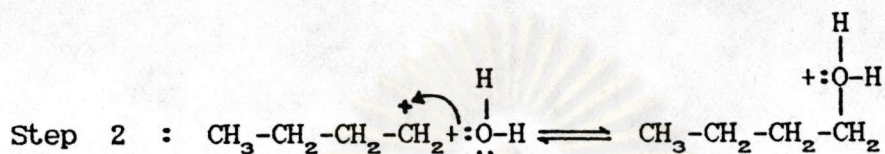
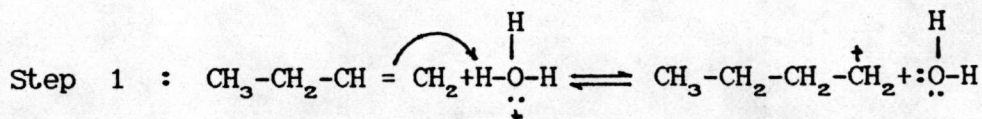


Hydration of n-butene to 2-butanol :



major product

Hydration of butene to n-butanol (minor product)



Generally at high temperatures n-propanol and n-butanol occurred as minor products vis-a-vis sec-butanol and iso-propanol. The reaction whereby alkenes are hydrated, or alcohols are dehydrated, is one in which the ultimate products are governed by chemical equilibrium. For example, if we want to dehydrate an alcohol, we must use a concentrated acid, so that the concentration of water is low (we often remove the water as it is formed, and it helps to use a high temperature). If we want to hydrate an alkene, we must increase the concentration of water (It also usually helps to use a lower temperature).

2.4 Thermodynamics of Isopropanol

The practical utilization of chemical thermodynamic data frequently is more readily achieved using pertinent functions tabulated at selected temperatures than using equations that require the user to calculate his own values at each temperature. Hence a

systematic digital computer method for compiling suitable tables is usually employed. The following information constitutes the basic data on each compound needed to prepare the thermodynamic property table:

1. Smoothed values of the ideal-gas heat capacity at 1 atm and nine temperatures (298.15°, 300°, 400°, 500°, 600°, 700°, 800°, 900° and 1000° k).

2. Practical entropy of the ideal gas at 1 atm and 298.15° K

3. The isothermal enthalpy for formation of the ideal gaseous compound at 1 atm and 298.15° K, from its elements in their reference states at 298.15° K

4. The identity and number of each type of constituent atom in the compound

5. Data on the reference element as follows : (a) gram atomic weight, (b) practical gram atom entropy value at each of the nine temperatures, and (c) gram atomic enthalpy value at each of the nine temperatures with the value zero assigned to 298.15° K to calculate entropies at 300° and 400° K. The Gibbs energy functions are next calculated from the relation:

$$-\frac{(G_T^\circ - H_{298}^\circ)}{T} = S_T^\circ - 1000 \frac{(H_T^\circ - H_{298}^\circ)}{T}$$

in which T is the absolute temperature and 1,000 is a conversion factor to convert kilocalories to calories. The enthalpies of formation are calculated from:

$$Hf_T^\circ = \Delta Hf_{298}^\circ + [H_T^\circ - H_{298}^\circ] (\text{compound}) \\ - \sum [H_T^\circ - H_{298}^\circ] (\text{elements}),$$

in which the summation is carried out over the constituent elements in the compound. The standard Gibbs energy of formation is calculated from the relation

$$\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ$$

Here ΔS_f° , the standard entropy of formation of the compound from its elements at T°K, is calculated from:

$$\Delta S_f^\circ = S^\circ_T (\text{compound}) - \sum S^\circ_T (\text{elements}),$$

in which the summation includes all of the elements making up the compound.

The common logarithm of the standard equilibrium constant in terms of pressure is calculated from the equation

$$\log_{10} K_p = \frac{-\Delta G_f^\circ}{0.004575845T}$$

Subsequently, using Item 1 data (heat capacities) at 400°, 500° and 600°K, the coefficients are solved to give enthalpy and entropy increments relative to 400°K. These are added to the 400°K value to give the new values at 500°K, and higher-temperature values of the ΔH_f° , ΔS_f° , and $\log_{10} K_p$ are calculated successively for each temperature up to 1000°K. The results are summarized in the following table.

Isopropanol (Ideal Gas State)

T °K	cal/(mol °K)			Kcal/mol			
	C_p°	S°	$-(G^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔG_f°	$\log_{10} K_p$
298	21.21	74.07	74.07	0.00	-65.15	-41.49	30.411
300	21.31	74.21	74.08	0.04	-65.18	-41.34	30.118
400	26.78	81.09	74.98	2.45	-66.65	-33.17	18.120
500	31.89	87.64	76.86	5.40	-67.82	-24.66	10.776
600	35.76	93.81	79.18	8.78	-68.74	-15.94	5.804
700	39.21	99.58	81.68	12.53	-69.46	-7.07	2.208
800	42.13	105.01	84.26	16.61	-69.99	1.87	-0.511
900	44.63	110.12	86.86	20.95	-70.36	10.88	-2.642
1000	46.82	114.94	89.43	25.52	-70.58	19.93	-4.355

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย