Overview of the Catalytic Production of Isoprene from different raw materials; Prospects of Isoprene production from bio-ethanol.

Abstract

Isoprene is a valuable monomer for the rubber and most chemical industries. The five carbon monomer is used to make synthetic latex similar to the natural and it is becoming a monomer of choice because of the possibility to manipulate its properties. The rapid development of synthetic rubber is a result of the huge demand for this material. Currently, SR is used practically in all spheres of industry and national economy with its global production exceeding 1.3 million tons per year In this paper, various methods for its production and their shortfalls were studied; the prospect for isoprene production from bio-ethanol was also highlighted.

Keywords

Isoprene • Synthetic rubber (SR) • Catalyst • Isopentane • Isopentene

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1. Introduction

For over 130 years now, isoprene has always been known to be the main component of natural rubber, however, before the 1940's not even one synthetic latex by the complexity of its properties could completely replace natural rubber. The situation changed dramatically after K. Ziegler and G. Natta discovered a new catalyst system for the stereospecific polymerization of unsaturated hydrocarbons, and by the efforts of various scientists from different countries (USA, USSR, Italy etc), effective methods for the synthesis of cis – 1-4- polyisoprene -a saturated analog and substitute of natural rubber, were developed [1].

The rapid development of synthetic rubber is a result of the huge demand for this material. Currently, SR is used practically in all spheres of industry and national economy with its global production exceeding 1.3 million tons per year [2].

According to the market research firm SRI consulting, Goodyear is one of the world's largest consumers of isoprene, using it to produce poly-isoprene - synthetic version of natural rubber. The enzymes company "Genecor" figures that the world's market for isoprene is worth as much as 2 billion USD per year [3].

Isoprene, a colourless volatile liquid with a characteristic odor, is a homologue of 1, 3 –butadiene, in which hydrogen at the second carbon atom is substituted with a methyl group CH_3 [4]. Under normal conditions isoprene is flammable and toxic. Its maximum permissible concentration in a work area is 40 mg/m³. It is practically insoluble in water, but soluble in alcohol, ether and other organic solvents [5].

Isoprene or 2- methyl – 1, 3 – butadiene has great significance as a starting monomer for the synthesis of stereoregular isoprene rubber due to the possibility of purposeful manipulation of its properties [6].

Below are some of the methods for isoprene synthesis used on an industrial scale;

1. Synthesis from Isobutylene and formaldehyde.
2. Dehydration of isopentane.
3. Oxidative dehydration of isopentane.
4. Synthesis from propylene.
5. Synthesis from acetylene and acetone.
6. Recovery of isoprene from C5 fraction of liquid petroleum pyrolysis.
7. Liquid phase oxidation of hydrocarbons.

Almost every one of these methods is available in several technical options. One reason for such a variety of methods of isoprene synthesis is as a result of the possibility of the use of many kinds of raw materials.

In Russia, methods 1, 2 and 6 are the commonly used whereas, in the US most isoprene is a by – product of the ethylene industry. However, one of the decisive factors in determining the prospects of a method for the synthesis of isoprene is the availability of resources and the cost of raw materials used [7]. Moreover, with the increasing scarcity of fossil fuels, issues with supply, the ever growing demands on the worlds natural resources coupled with " man made" global warming due to CO_2 emissions, it has become imperative to investigate sustainable and carbon neutral alternatives to fossil fuels [8]. Due to political incitements as well as emerging tax policies, there is huge incentive to the use of monomers of a biological origin. Ethanol is one of the most relevant potential sources of bio – carbon today. Production of bioethanol occurs via fermentation of sugars and

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corn feedstocks, while the second generation bioethanol from lignocellulosic feedstock is under extensive development [9].

In this paper, the most common industrial methods of isoprene production and their shortfalls were studied; the possibility of isoprene production from ethanol was also highlighted.
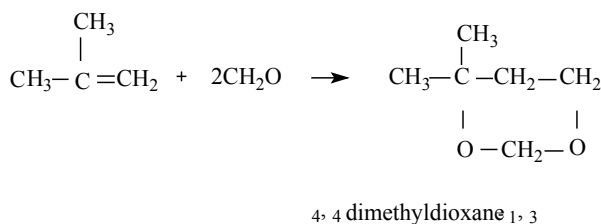
2. Synthesis methods

2.1. Extraction of isoprene from C5 fraction of liquid petroleum pyrolysis.

This is the simplest method of isoprene production which involves its extraction from C5 fraction of liquid petroleum pyrolysis containing about 15 – 20% isoprene. This fraction is produced as a by – product in the production of ethylene and propylene. However, the transportation of raw materials from different refineries for the industrial realization of this method creates some difficulties [1]. Environmental issues are also there to be tackled especially with the recent tightening of environmental laws.

2.2. Two step isoprene production from isobutylene and formaldehyde

The reaction of unsaturated hydrocarbons with formaldehyde was first described by H. Prince in 1917, he studied the reaction of styrene and formaldehyde in the presence of sulfuric acid as the catalyst, which resulted to the formation of formals of dioxane -1, 3. Fitski and Friedrickson in 1932 discovered the possibility of using princes reaction for the synthesis of diene hydrocarbons. In 1946, soviet scientists M. I. Farberov and M. S. Nemtsov et. al discovered the possibility of developing highly efficient process for isoprene production using this method. The method was actualized and implemented in 1964.

The synthesis of isoprene using this method is carried out in two steps. In the first step, isobutylene is condensed with formaldehyde in the presence of an acidic catalyst such as diluted sulphuric acid to form 4, 4- dimethyldioxane -1,3 as depicted below.

$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 \ + \ 2CH_2O \ \longrightarrow \ CH_3-\underset{\underset{O-CH_2-O}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{}{CH_2}-CH_2$$

4, 4 dimethyldioxane 1, 3

In the second step, 4 - 4- dimethyldioxane -1, 3 is decomposed into isoprene on a solid phosphate catalyst such as calcium phosphate.

$$CH_3-\underset{\underset{O-CH_2-O}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_2 \ \longrightarrow \ CH_2=C-CH=CH_2 \ + \ CH_2O \ + \ H_2O$$
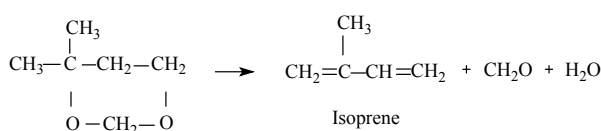
Isoprene

In each of these steps, the main reaction is accompanied by numerous side reactions. In the first step, as a result of the side reactions, trimethyl carbinol, methylal, dioxane alcohols, diols, ethers etc, are formed. The formation of isoprene in the second step is also accompanied with the decomposition of dimethyldioxane to iso- butylenes and formaldehyde, dihydromethylpyran, hexadiene, piperylene, terpene compounds, green oil etc.

Isobutylene contained in C5 fraction of liquid hydrocarbon pyrolysis is the raw material mainly used. However, the presence of n- butane compounds and butadiene leads to the formation of isomeric dioxane compounds which decompose to a wide range of by- products.

The second step of isoprene synthesis from isobutylene and formaldehyde is carried out in a section type reactor using energy from steam heated to 973K. Acid phosphates of group II metals are used as catalysts, calcium phosphate in particular. The selectivity of phosphate catalyst is increased by its continous activation in the process, by the introduction of small amounts of phosphoric acid vapour directly into the catalysis zone which leads to the formation of acidic phosphates on the surface of the calcium phosphate catalyst.

$$Ca_3(PO_4)_2 + H_3PO_4 \rightarrow 3CaHPO_4$$

During catalysis, coke is deposited on the surface of the catalyst, this is the reason for which regeneration is done every 2 -3 hrs by burning off the coke in a stream of air mixed with steam at temperatures above 773K. The process flow diagram of isoprene production from the decomposition of dimethyl dioxane is shown in the figure below.

Dimethyldioxane vapour is mixed with steam and sent to reactor (2) to which steam heated to 973K from the the steam heater (1) is supplied. The gas mixture enters the cascade of heat exchangers (3), in which the products are condensed. The condensate consisting of two phases –the organic and aqueous, is allowed to settle in (4). The oily layer gets washed out in (5) where the extraction of dissolved formaldehyde takes place. The washed stream is sent to rectification column (6), where the lighter products, mainly isobutylene and isoprene are separated from the decomposed dimethyl dioxane and other less volatile substances. The stream from (6) then enters the rectification column (7), where highly concentrated isobutylene is collected and returned for synthesis of dimethyl dioxane. The distillate from (7) – raw isoprene is sent to columns 8, 9 for further rectification in order to remove impurities with high boiling points, mainly cyclopetadiene and carbonyl compounds, which are washed out in colum (10). The distillate from column (11) is sent to vacuum column (12) in which by-products with high boiling points, mainly isoprene oligomers or green oil from the second stage of the synthesis are removed from the recycled dimethyldioxane. An extragent (made up of the mixture of iso-propyl alcohol and dimethyldioxane) can be recovered for the extraction of the byproducts of the first stage of the process from the recycled dimethyldioxane, by rectification.

The contact gas from the reactor goes for condensation, while the condensate is sent to the settler where stratification into oily and aqueous layers is carried out. The oily layer undergoes rectification in a double column system, which gives
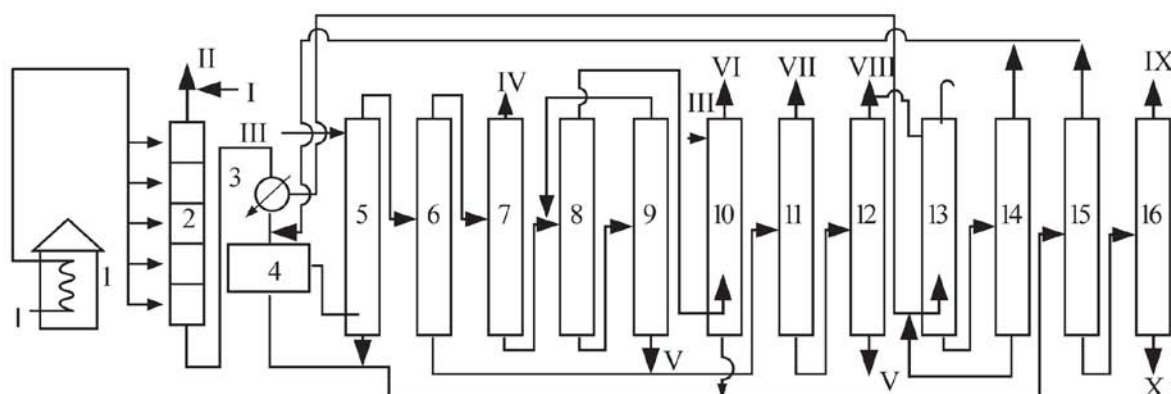
Figure 1. *Flow diagram of isoprene production from dimethyl dioxane decomposition. [1]*
1-Steam heater, 2- reactor, 3 – condenser, 4-settler, 5, 10 – columns for washing, 6 – crude isoprene distillation column, 7 – distillation column for recycled iso – butylenes, 8, 9 – column for isoprene rectificate, 11- MDGP fraction column, 12 – recycled DMD column, 13 - absorber, 14 – desorber, 15 – distillation column for light organic compounds, 16 – recovery column for formaldehyde.
Streams
I steam, II- DMD Vapour, III – washing water, IV- recycled isobutylene, V- boiling impurities, VI- isoprene rectificate, VII- MDGP fraction; VIII – recycled DMD; IX- recovered formaldehyde, X- waste water.

yields to iso- butylenes (which is returned to the first stage of the synthesis), fraction of raw dimethyl dioxane, and isoprene distillate which contains traces of carbonyl compounds (mainly aldehydes). The raw isoprene is sent for rectification (distillation), in order to get isoprene distillate, which is further rinsed with condensate in order to get rid of carbonyl compounds. Finally, polymerization inhibitors are added to prevent the polymerization of isoprene in the distillation columns.

2.2.1. Advantages of the method

One of the major advantages of this method in comparison with others is the production of a product with high purity and with relatively simple methods of synthesis and purification employed. Below, in Table 1 is the composition of the isoprene distillate in %wt.

Table 1. Composition of the isoprene distillate. [1]

Compound	%wt
Isobutylene	0,006
Isopentane	0,002
Isoprene	99,69
Methylcyclobutane	0,0002
Trimethylethylene	0,10
Isopentene	0,18
Acetylene compounds	0,00015
Cyclopentadiene	0,0001
Carbonyl compounds	0,00033

2.2.2. Disadvantages

One of the major disadvantages of this process is the formation of numerous by products up to 0,5 ton/ton isoprene. In order to utilize some of the byproducts, trimethyl carbonyl fraction undergoes decomposition which leads to the formation of isobutylene that is recycled into the process which significantly reduces its consumption relative to 1 ton of isoprene. The decomposition of dihydromethylpyran fractions allows for the production of additional 2% of isoprene.

The need for the recovery of formaldehyde formed during the decomposition or cracking of dimethyloxidane is another shortfall but it can be taken care of by using a process in which intermediate products like methylbutanediol or isoamylene alcohols are formed, which can easily be converted to isoprene with high yields at relatively mild conditions (453 – 527 K) on phosphate catalysts. However, the development of an industrial process which inculcates the formation of these intermediate compounds is hampered by the absence of methods for their selective production.

A more successful way of isoprene production through methylbutanediol formation stage was developed by the Russian institute of organic chemistry in collaboration with All – unioin scientific research and design institute of monomers in Tula, Russia [1].

2.3. Isoprene production via the dehydrogenation of C5 hydrocarbons.

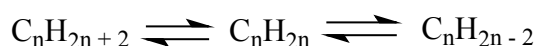### 2.3.1. Two-step dehydrogenation of isopentane into isoprene

Catalytic dehydrogenation of saturated, unsaturated or alkyl aromatic hydrocarbons is the main industrial method for the production of butadiene, isoprene and styrene. Dehydrogenation can be done in two ways; one step and two

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step methods. In the two step method, isopentane in the first stage is dehydrogenated to isoamylene, which are further dehydrogenated to isoprene in the second stage of the process as shown below:
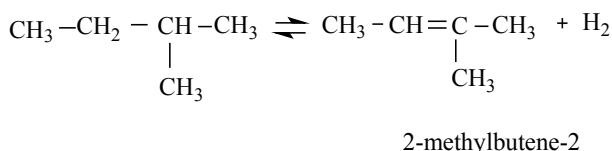
$$iso-C_5H_{12} \rightleftharpoons iso-C_5H_{10} + H_2$$

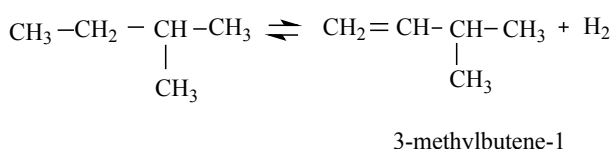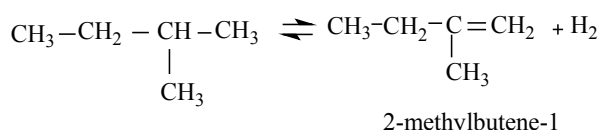$$iso-C_5H_{10} \rightleftharpoons iso-C_5H_8 + H_2$$
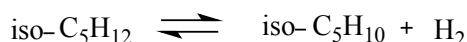
one- step method is different from the two step in the sense that the dehydrogenation of isopentane and isopentane-isoamylene mixtures is carried out on the same catalyst without intermediate separation of isopentane and isoamylenes. An important advantage of the two-step process is the possibility of the use of highly selective catalyst at each stage and high energy consumption significantly undermines the competitiveness of the two-step method in comparison with the one- step method.

The dehydrogenation of alkanes, isopentane in particular is a reversible endothermic reaction.

$$C_nH_{2n+2} \rightleftharpoons C_nH_{2n} \rightleftharpoons C_nH_{2n-2}$$

Alongside the dehydrogenation of isopentane, the following reactions also occur:

$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3 \rightleftharpoons CH_3-CH_2-\underset{\underset{CH_3}{|}}{C}=CH_2 + H_2$$

2-methylbutene-1

$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3 \rightleftharpoons CH_2=CH-\underset{\underset{CH_3}{|}}{CH}-CH_3 + H_2$$

3-methylbutene-1

$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3 \rightleftharpoons CH_3-CH=\underset{\underset{CH_3}{|}}{C}-CH_3 + H_2$$

2-methylbutene-2

In this case three isomers of isopentene; 2-methyl butene-1, 3-methylbutene-1 and 2 methyl butene are formed. However 3 – methylbutene is about 65% of the products formed. In addition to the formation of isomers, a large number of other side reactions occur but the most important ones are as follows:
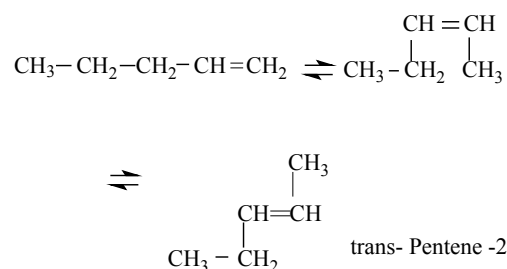- Skeletal isomerization of isopentane

$$iso-C_5H_{12} \rightleftharpoons n-C_5H_{12}$$
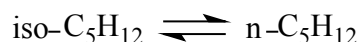
- Isomerization with the migration of double bonds in isopentene.
2-methylbutene = 1 3-methylbutene-1 = 2-methybutene-2;

- Isomerization with the migration of double bonds in pentene.

$$CH_3-CH_2-CH_2-CH=CH_2 \rightleftharpoons CH_3-\underset{\underset{CH=CH}{|}}{CH_2}\; \underset{CH_3}{|}$$

$$\rightleftharpoons \underset{CH_3-CH_2}{\overset{CH_3}{\underset{|}{CH=CH}}} \quad \text{trans- Pentene -2}$$

- Cracking of the feed substance, intermediate, and final products.
- Deeper dehydrogenation accompanied by cyclization, aromatization and formation of compounds with triple bonds;
- Reaction of olefins, diene hydrocarbons and water vapour resulting to the formation of oxy- compounds;
- Coke formation.

The dehydrogenation of isopentane to isopentene is also accompanied by the formation of light hydrocarbons of C1 – C4, heavier of C6 and above, CO, CO_2 and coke. The production of isoprene from isopentane in comparison with the production of butadiene is more complicated by the fact that a larger amount of isomers are formed in this process than those formed during the dehydrogenation of butane.

Shortfall of the method

Isopentane and isopentene which posses the hydrocarbon skeleton of the final product are scarce due to their wide usage as high quality gasoline additive instead of tetraethyl lead. This limits their usage for isoprene production.

Technological overview of isopentane dehydrogenation into isopentene

There are various technological options of the above mentioned process amongst which are;
- Dehydrogenation in an adiabatic reactor with a fludized catalyst bed
- Dehydrogenation in a fluidized bed with pulverized catalyst

Catalyst

The process is carried out on Al-Cr-Li, Al-Cr-Pb catalyst system promoted on K_2O. Al- Cr-Li, Al-Cr-Pb, Al-Cr-Zn systems are more active than Al-Cr system promoted on K_2O. The process flow diagram of isopentane dehydrogenation in fluidized (boiling) pulverized catalyst developed and implemented in a semi industrial scale at the research institute of monomers for synthetic rubber, Yaroslav, Russia is as shown below.

Dehydrogenation of isopentene to isoprene (stage-2)

$$iso-C_5H_{10} \rightleftharpoons iso-C_5H_8 + H_2 + \triangle H$$
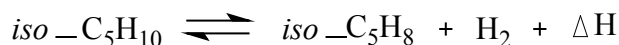
This process is a reversible endothermic reaction. The industrial dehydrogenation of iso-pentene is carried out on solid catalysts
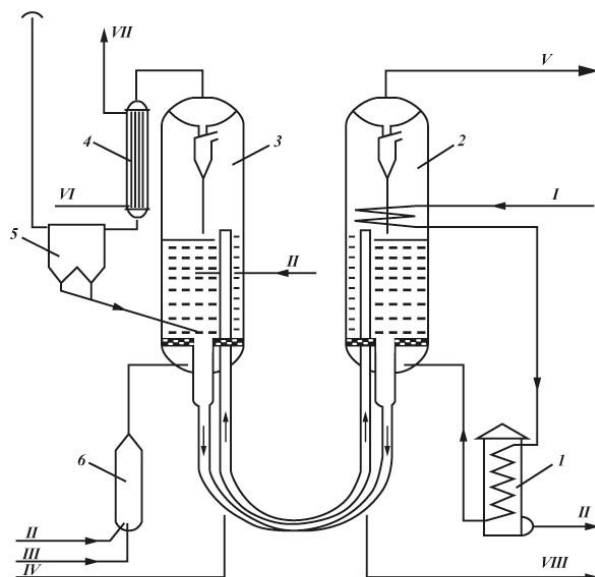
*Figure 2.* Process flow diagram for isopentane dehydrogenation in a boiling layer of pulverized catalyst [1].
1 – heater; 2 –reactor; 3 – regenerator; 4 –recovery boiler; 5 – electric filter; 6 – burner.
Streams: I – Isopentane; II –fuel; III – air under pressure; IV – air for transportation of catalyst, V– contact gas; VI – steam condensate; VII – steam; VIII – Nitrogen for transportation of catalys

with oxides of iron and chromium as the active elements. A typical composition of Cr-Fe-Zn system (in %mol) is as follows; CrO_3 – 0,5, Cr_2O_3 – 5-6, ZnO- 2 – 4, Fe_2O_3 – 15 -17, $ZnCr_2O_4$ – 45 -50, $FeCr_2O_4$ – 20 -25

2.3.2. One- step dehydrogenation of isopentane into isoprene

The production of isoprene via the two- step process in contrast to the one-step process is carried out in two different reactors and on different catalyst which invariably complicates and increases the cost of the process. In addition to these, the separation of isopentane – isopentene mixtures is a big problem which is absent in the one-step method. One – step dehydrogenation of isopentane into isoprene is an endothermic process, in which the dehydrogenation of isopentane to isopentene and the formation of isoprene from isopentene occur simulteanously. The yield of the main product is controlled by the thermodynamics of the process.

$$iso-C_5H_{12} \rightleftharpoons C_5H_8 + 2H_2$$
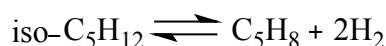
At atmospheric pressure and temperature of about 773K, the quantity of isoprene in the equilibrium mixture of isopentane-isopentene –isoprene is less than 1% but at 873K the isoprene content reaches 10%. Increase of the equilibrium content of isoprene is favoured by the the reduction of the partial pressure of the hydrocarbon source. Thus, at a temperature of about 800 and a partial pressure of 0.02 MPa, the equilibrium mixture

contains about 10% of isoprene and at the same pressure and temperature of 873K, the fraction of isoprene increases to 33%. Lowering the partial pressure of the hydrocarbon can be achieved not only by conducting the reaction under vacuum, but also by diluting the feedstock with an inert diluent such a steam. Thus, the thermodynamically favourable conditions of dehydrogenation of isopentane to isoprene are high temperature (above 900K) and low partial pressure of isopentane vapour in the reaction mixture.

One-step production of isoprene by dehydrogenation includes dehydrogenation of isopentane, the release of C5 hydrocarbon fraction from the contact gas, formation of concentrated isoprene and its subsequent purification.

Dehydrogenation of isopentane – isopentene mixtures into isoprene is carried out at reduced partial pressure of hydrocarbons, which is achieved by using an inert diluents or creating a vacuum in the reactor.

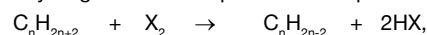### Advantage over the two-step process

The simplicity of the equipment and technological design of the process with regenerative cycle results to low capital investment and operational cost, flexibility of the process in respect to raw materials since C5 hydrocarbon fraction of any composition can be processed on the same plant. In Russia, the process was developed by the firm Yarsintez in Yaroslavl, Russia.

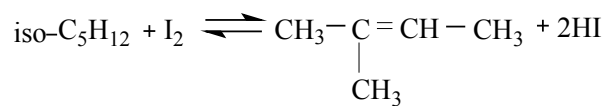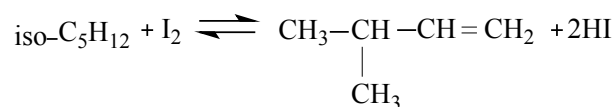### 2.4. Oxidative dehydrogenation of isopentane to isoprene

Two stage oxidative dehydrogenation of isopentane into isoprene

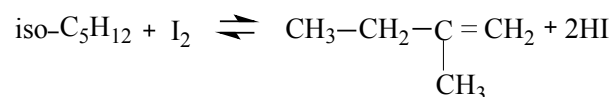Below are the reactions that occur during the oxidative dehydrogenation of isopentane:

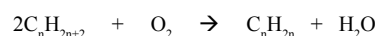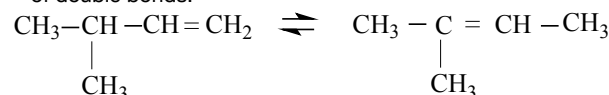1. Dehydrogenation of isopentane to isopentene (iso-amylenes)

$$C_nH_{2n+2} + X_2 \rightarrow C_nH_{2n-2} + 2HX,$$
Where X = O, I, Cl, Br

$$iso–C_5H_{12} + I_2 \rightleftharpoons CH_3-CH-CH=CH_2 + 2HI$$
$$\qquad\qquad\qquad\qquad\qquad | $$
$$\qquad\qquad\qquad\qquad\quad CH_3$$

$$iso–C_5H_{12} + I_2 \rightleftharpoons CH_3-C=CH-CH_3 + 2HI$$
$$\qquad\qquad\qquad\qquad\quad | $$
$$\qquad\qquad\qquad\qquad CH_3$$

cis- trans- isomers

$$iso–C_5H_{12} + I_2 \rightleftharpoons CH_3-CH_2-C=CH_2 + 2HI$$
$$\qquad\qquad\qquad\qquad\qquad\quad | $$
$$\qquad\qquad\qquad\qquad\qquad CH_3$$

Or, if X = O, then
$$2C_nH_{2n+2} + O_2 \rightarrow C_nH_{2n} + H_2O$$
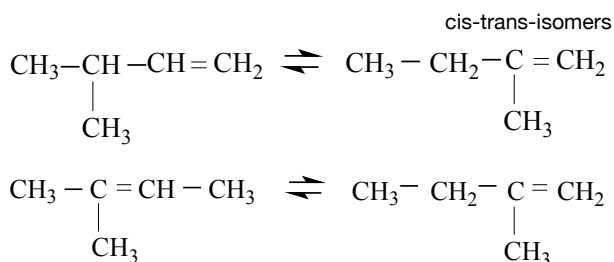
2. Isomerization of isopentene (isoamylenes) with the migration of double bonds.

$$CH_3-CH-CH=CH_2 \rightleftharpoons CH_3-C=CH-CH_3$$
$$\qquad\quad | \qquad\qquad\qquad\qquad\qquad | $$
$$\qquad\quad CH_3 \qquad\qquad\qquad\qquad\quad CH_3$$

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cis-trans-isomers

$$CH_3-CH-CH=CH_2 \rightleftharpoons CH_3-CH_2-C=CH_2$$
$$|CH_3 |CH_3$$

$$CH_3-C=CH-CH_3 \rightleftharpoons CH_3-CH_2-C=CH_2$$
$$|CH_3 |CH_3$$

3. Dehydrogenation of isopentene

$$CH_3-CH-CH=CH_2 + X_2 \rightleftharpoons iso\text{-}C_5H_8 + 2HX$$
$$|CH_3$$

$$CH_3-C=CH-CH_3 + X_2 \rightleftharpoons iso\text{-}C_5H_8 + 2HX$$
$$|CH_3$$

$$CH_3-CH_2-C=CH_2 + X_2 \rightleftharpoons iso\text{-}C_5H_8 + 2HX$$
$$|CH_3$$
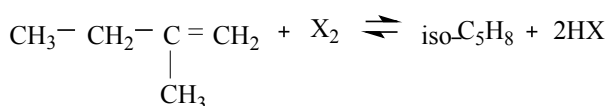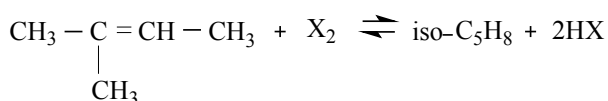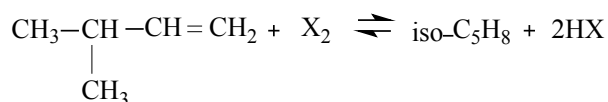
4. Skeletal isomerization of isopentane and isopentene, hydrocarbon cracking and combustion of hydrocarbons

Advantages of this process

The main advantage of oxidative dehydrogenation of C4 and C5 hydrocarbons for the production of butadiene and isoprene which is, its practical irreversibility and the absence of thermodynamic limitations can significantly increase yields of dienes and allow the process to be conducted at lower temperatures than those of the ordinary dehydrogenation.

The first reports about the use of oxygen in the dehydrogenation of olefins appeared in 1934 – 1935. Prior to the mid 1960's, catalyst for oxidation and ammoxidation of hydrocarbons such as bismuth – molybdenium and tin – antimony catalyst were used. Further research lead to the development of two types of catalyst; catalysts based on Iron. The catalyst system for the oxidative dehydrogenation of olefins, which are bismuth phosphate and bismuth tungstate were proposed at the end of 1959, but at the beginning of 1960, molybdenum oxide (or other compounds of molybdenum) promoted by bismuth oxide were suggested. Furthermore, phosphates, molybdates, tungstates of indium or its oxides on supports, and also catalysts consisting of oxides of molybdenum, titanium, antimony, bismuth, copper, cobalt, tin, lead, cadmium, their salts or mixtures of salts with oxides of phosphorus, bismuth and tellurium were proposed for the oxidative dehydrogenation of olefins. From 1964, extensive research on the development of catalysts based on ferrites of metals such as magnesium, calcium, zinc, strontium, cadmium, barium, manganese, cobalt and nickel for the oxidative dehydrogenation of olefins were conducted. The yield and selectivity on the best catalysts samples were found to be 65-70% and 90% respectively.

The most efficient hydrogen acceptor is iodine. Iodine simultaneously catalyzes the dehydrogenation process.

However, the stoichiometry of the reaction is such that the formation of 1 mole of isoprene requires 2 moles of iodine, which invariably makes the realization of this process economically infeasible. Iodine consumption can be greatly reduced by converting hydrogen iodide to elemental iodine in the reaction and this can be done effectively with the introduction of oxygen to the reaction.

$$2HI + 0{,}5O_2 \rightarrow I_2 + H_2O$$
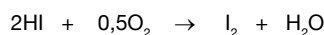
This reduces not only iodine consumption, but also increases the selectivity of the entire process. However, oxidative dehydrogenation using iodine in the presence of oxygen does not completely solve the problem of iodine consumption since the quantity of iodine compounds formed is large. A more effective way to reduce the consumption of iodine is by the use of solid hydrogen acceptors. The acceptors react with hydrogen iodide in either of the following ways:

$$MO + 2HI \rightarrow MI_2 + H_2O$$
Or
$$M(OH)_2 + 2HI \rightarrow MI_2 + 2H_2O$$
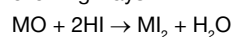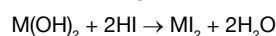
Oxides and other compounds of alkali and alkaline earth metals, transition metals and others in melted forms or deposited on solid inert supports such as alumina, silica gel etc, can be used as iodine acceptors. These acceptors are then withdrawn from the reaction zone and are subjected to treatment using pure oxygen or air:

$$2MI_2 + O_2 \rightarrow 2MO + 2I_2$$
$$2MI_2 + O_2 + 2H_2O \rightarrow 2M(OH)_2 + 2I_2$$
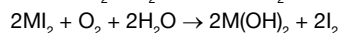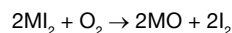
The released iodine and regenerated catalyst is returned to the reaction zone. In this process of dehydrogenation with iodine, a high selectivity value is achieved, which is as a result of the inhibition of cracking and deep oxidation of hydrocarbons by iodine. This kind of process is implemented in the industry.

Oxidative dehydrogenation of isopentene (2nd stage).

In contrast to the oxidative dehydrogenation of butenes, the oxidative dehydrogenation of isopentene (isoamylenes) into isoprene did not receive significant attention and invariably not further developed. The selective catalysts for this process are oxides of iron, vanadium, molybdenum and magnesium. The common pattern of changes in the activity of metal oxides in the oxidative dehydrogenation of n-butenes allows for the presumption that the known effective catalysts of oxidative dehydrogenation of n-butene will also catalyze the oxidative dehydrogenation of isoamylenes. Iron phosphates with a stoichiometric excess of phosphorus is used as catalyst. Isoprene yield and selectivity is 70 – 80% and 80 – 90% respectively. It is also important to note that ferrites of magnesium and magnese, molybdenium – antimony, uranium – antimony, tin – antimony, bismuth – molybdenum catalysts have good catalytic properties.
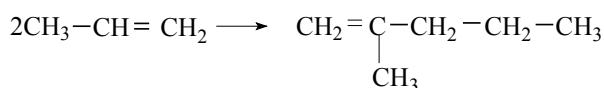
2.5. Isoprene production from propylene

The synthesis of isoprene from propylene was first suggested by Gorin and Oblad in 1946. The process involves the dimerization of propylene of propylene on aluminosilicate catalyst, followed

by the thermal cracking of the dimer. The yield of isoprene was however low but interests in this process was revived in the 1960's.

Isoprene synthesis by the dimerization of propylene gained practical attention after the discovery of selective oligomerization of lower olefins in the presence of organoalumininum catalysts by K. Ziegler. Dimerization of propylene in the presence of solid acid catalysts takes place by the mechanism of cationic oligomerization of olefins. In this case, a mixture of isomeric dimmers are formed from which isoprene is obtained by the pyrolysis of 2-methylpentene -2. This process includes the following steps;

1. Dimerization of propylene to form 2-methylpentene-1

$$2CH_3-CH=CH_2 \longrightarrow CH_2=\underset{\underset{CH_3}{|}}{C}-CH_2-CH_2-CH_3$$

2 Isomerization of 2-methylpentene-1 to 2-methylpentene -2

$$CH_2=\underset{\underset{CH_3}{|}}{C}-CH_2-CH_2-CH_3 \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CH_3$$
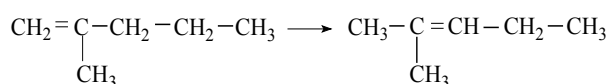
3 Demethanation (cracking) of 2-methylpentene-2 with the formation of isoprene.

$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CH_3 \longrightarrow CH_2=\underset{\underset{CH_3}{|}}{C}-CH=CH_2 + CH_4$$
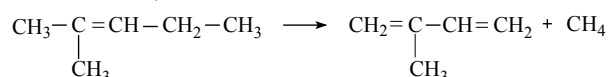
Figure 3 below shows the basic process flow diagram for isoprene from propylene production implemented by Goodyear scientific design method

1.Dimerization reactor, 2- evaporation column, 3-rectification column, 4- isomerization reactor; 5-separation column; 6-reactor for initiated cracking

Streams

I propylene; II- catalyst solution, III- residual oil; IV – 2 – methyl pentene – 1; V- 2-methylpentene-2; V- isoprene.

The raw material used is propane – propylene fraction, which is pre-dried and purified. The reactor unit consists of two units. At the exit of reactor (1), the feed mixture is throttled to a pressure level close to atmospheric, condensed in the cooling units and then fed to the separation units. Conversion of propylene in the described conditions is 70 – 85% at 97% yield of dimmers based on the reacted olefin. The condensed feed enters the evaporation column (2), where the catalyst is separated from higher oligomers of propylene which accumulate in the system as a result of continuous operation. A small portion of the catalyst (tripropyl-aluminum) is removed from the reactor and replaced with freshly prepared catalyst and sent for regeneration due to poisoning and thermal decomposition. 2-methylpentene-1, along with other light hydrocarbons and unreacted propylene is distilled from the top of the evaporation column (2) and enters the rectification column (3), where the separation of low boiling hydrocarbons takes place. 2-methyl pentene goes through a system of rectification columns and then into the reactor (4) for isomerization.

Isomerization of 2-methylpentene-1 into 2-methylpentene is conducted in the gaseous phase at a temp range of 423 – 573K and a flow rate of 0,15 – 0,5 L/L(kat)/h over a fixed bed of solid catalyst at atmospheric pressure. The reaction mixture enters the pyrolysis furnance (6) to which over heated steam is also fed. Furthermore, the separation of the hydrocarbon and aqueous phases take place with hydrogen bromide dissolved in the later. Aqueous solution of hydrogen bromide is mixed again with fresh feed. Methane and light hydrocarbons are released from the hydrocarbon fraction while the target fraction is sent for purification and subsequently the separation of isoprene.

Disadvantage

The disadvantage of this method is the low efficiency of the process of pyrolysis: Isoprene yield does not exceed 50 – 60%, and therefore the overall yield of isoprene is 45 – 50 %. In the industry, this method is used on a limited scale.
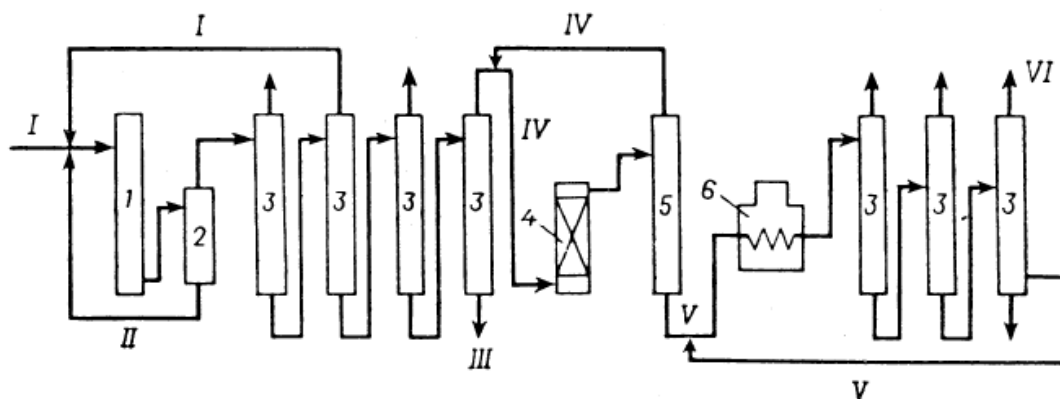

Figure 3. *Process flow diagram for isoprene from propylene production implemented by Goodyear scientific design method.* [1]

Overview of the Catalytic Production of Isoprene from different raw materials; Prospects of Isoprene production from bio-ethanol.

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2.5.1. Isoprene synthesis from ethylene and propylene

The possibility of obtaining isopentene and subsequently isoprene from ethylene and propylene was proved by Ziegler et al. The process was carried out in two stages. In the first stage, reaction between alkyl-aluminum and propylene takes place with the formation of diethyl-isopentyl-aluminum at approximately 473K and 2,0 MPa. In the second stage, diethyl-isopentyl-aluminum reacts with the remaining ethylene at room temperature and average pressure. Light hydrocarbons separated from the reaction mixture by rectification which is composed of 80 – 85 % of 2-methylbutene-1, undergoes dehydrogenation with the formation of isoprene.

Disadvantage

The main set back of this process is the large number of circulating organoaluminum compounds which makes the process presently infeasible for industrial application.

2.6. Isoprene from acetylene and acetone

The first attempt to synthesize isoprene from acetylene and acetone was made by Merling in 1914. He conducted the condensation of acetylene with acetone through dimethylethylcarbinol and subsequently obtained isoprene. However, due to the stagnation in the development of the method at that time, it was not implemented in the industry. Interests in this method was revived in the 1930's when A. E. Favorskyi et al again conducted the condensation of acetone with acetylene and proposed an industrial method for isoprene production. However, this method had a number of shortcomings that inhibited its implementation in the industry especially the low selectivity of the second stage of the process and the use of explosive solvents such as ethers at the condensation stage of acetylene and acetone. Subsequently, the Italian company SNAM improved this method.

The synthesis of isoprene using Favorskyi's method is made up of 3 stages. In the first stage, condensation of acetylene with acetone (ethylization) takes place with the formation of dimethylacetynyl carbinol. Firstly, potassium acetylide is formed alongside the formation of a monohydrate of KOH as a result of water molecules bonding with the unreacted KOH as shown below:

$$HC{\equiv}CH \ + \ KOH \quad \rightarrow HC{\equiv}CK \ + \ H_2O \ ,$$
$$KOH \ + \ H_2O \rightarrow KOH \cdot H_2O.$$
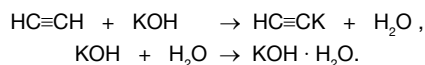
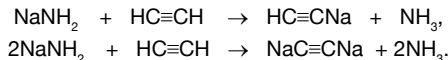Then potassium acetylide reacts with acetone to form dimethylacetynylcarbinol:
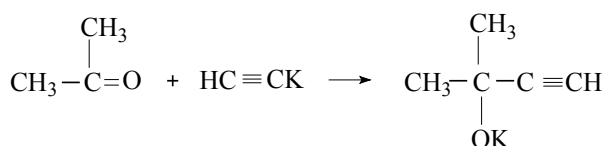
Hydroxides of other metals in these conditions do not react with acetone and cannot catalyze ethylization reaction.

A method was developed using liquid ammonium solvent. In this case, the catalyst is sodium amide, which is formed by the reaction of sodium metal and ammonia
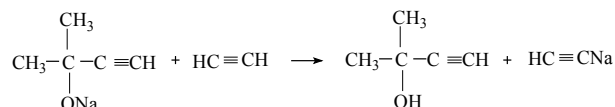
$$2Na + 2NH_3 \ \rightarrow \ 2 \ NaNH_2 + H_2.$$
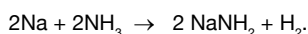
In the presence of excess acetylene, mono or disodium acetylene is formed.

$$NaNH_2 \ + \ HC{\equiv}CH \ \rightarrow \ HC{\equiv}CNa \ + \ NH_3,$$
$$2NaNH_2 \ + \ HC{\equiv}CH \ \rightarrow \ NaC{\equiv}CNa \ + 2NH_3.$$
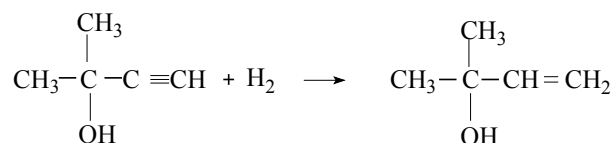
In liquid ammonia, sodium acetylide reacts with acetone to form an alcoholate of dimethylacetynylcarbinol.
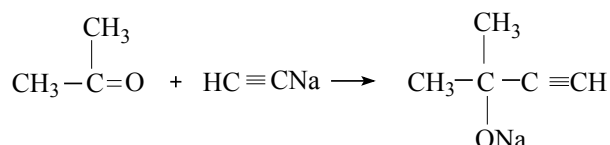
The alcoholate is then reduced in excess acetylene:

In the second step of the process, dehydrogenation of dimethylacetynylcarbinol (methylbutynol) to dimethylvinylcarbinol (methylbutenol):


Colloidal palladium on a carrier is used as the catalyst source. The hydrogenation of methylbutynol is conducted in a liquid phase at a temperature range of 303 – 353K and 0. 5 – 1 MPa. The selectivity of 99 – 99,5 % is achieved in the presence of an inhibitor which allows for complete conversion of methylbutynol to methylbutenol.

In the third step of isoprene synthesis by Favorskyi's method, catalytic dehydration of methylbutenol is carried out as shown below:
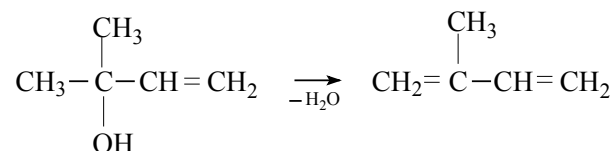
The dehydration process of dimethylvinylcarbinol proceeds with complete conversion (~97%) and selectivity of 99,8%. The produced isoprene is about 98,5% pure and does not require further purification, since it does not contain harmful contaminants and can be sent for stereospecific polymerization. Methylbutynol can also be converted into isoprene through iso-propenyl acetylene formation stage. The reaction takes place at 553K on aluminum phosphate catalyst
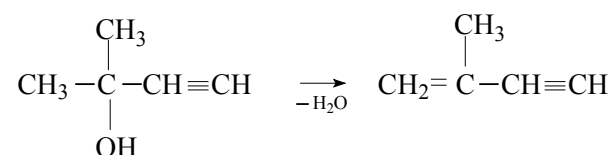
As a result of the hydrogenation of the triple bond of iso-propenyl acetylene, Isoprene is produced.

$$CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH\equiv CH \xrightarrow{H_2,\ Fe} CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH=CH_2$$
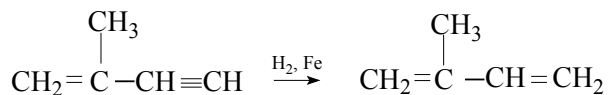
Advantage
The advantage of this process is the possibility of conducting it under mild conditions.
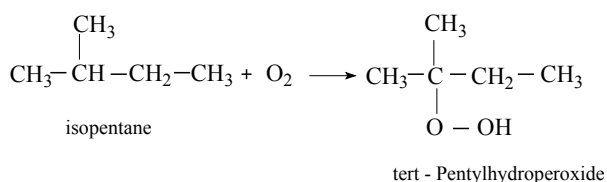
Disadvantage
The high cost of raw materials and the problems associated with the explosive nature of acetylene. Industrially, this method is rarely implemented.
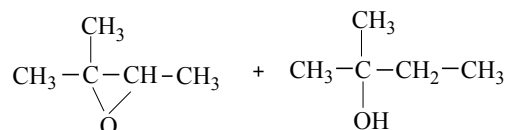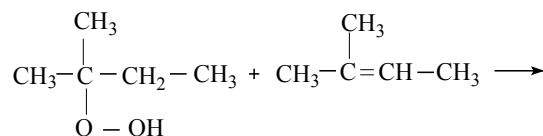
2.7. Isoprene production via Liquid phase oxidation of hydrocarbons.

Isoprene production via liquid phase oxidation of isopentene is based on its epoxidation using organic hydroperoxide. The process in the early 1960's was developed by an American firm "Halcon". It consists of 4 stages:

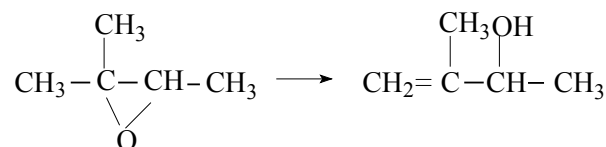1. Isopentane oxidation by atmospheric oxygen to tert- pentyl hydroperoxide:

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_3 + O_2 \longrightarrow CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle O-OH}{|}}{C}}-CH_2-CH_3$$

isopentane

tert - Pentylhydroperoxide

2. Reaction of hydroperoxide with 2-methylbutene-2, which is and intermediate product of the process, and then the production of 2-methylbutene-2 oxide.
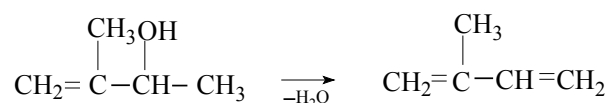
$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle O-OH}{|}}{C}}-CH_2-CH_3 + CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_3 \longrightarrow$$

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle O}{\diagdown\ \diagup}}{C}}-CH-CH_3 \quad + \quad CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_2-CH_3$$

2 - methylbutene - 2 Oxide   tert - Pentyl alcohol

3. Isomerization of 2-methylbutene-2-oxide to 2-methyl-1-ol-3

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle O}{\diagdown\ \diagup}}{C}}-CH-CH_3 \longrightarrow CH_2=\overset{\overset{\displaystyle CH_3OH}{|}}{C}-CH-CH_3$$

4. Dehydration of the alcohol to isoprene:

$$CH_2=\overset{\overset{\displaystyle CH_3OH}{|}}{C}-CH-CH_3 \xrightarrow{-H_2O} CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH=CH_2$$

The flow chart for the process is shown in the Figure 4.
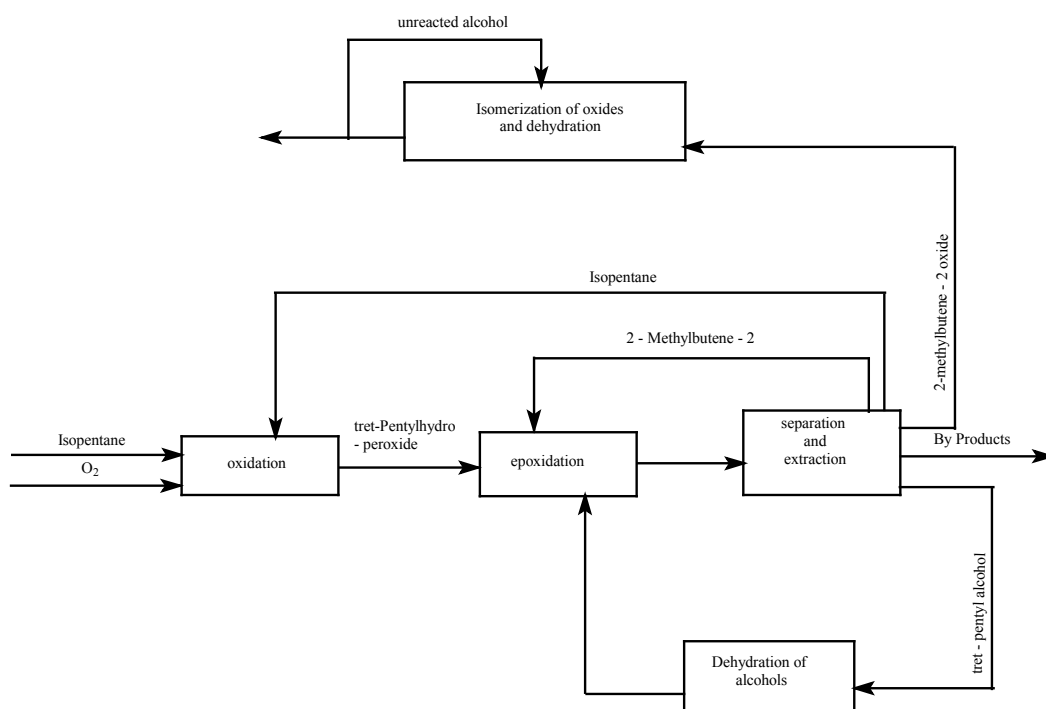
Figure 4. Flow chart for the process of isoprene production via Liquid phase oxidation of hydrocarbons.

Overview of the Catalytic Production of Isoprene from different raw
materials; Prospects of Isoprene production from bio-ethanol.

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3. Prospects of isoprene production from ethanol

The depletion of oil reserves due to over dependence on fossil fuels, issues related to the environment and climate changes have necessitated the exploration of other alternative and sustainable resources. Ethanol is a renewable and potential source of bio-carbon today which can be used to produce wide range of chemicals and bulk petrochemicals.

3.1. Bio-ethanol the potential feedstock for Isoprene production.

Production of bio-ethanol is a prospective way to reduce both the consumption of hydrocarbons of fossil sources and environmental pollution [9]. The desire to produce bulk chemicals in a sustainable way and the availability of low-cost bio-ethanol in large volumes has, however, resulted in a wave of petrochemical production from this commodity. Ethanol is a renewable energy source because the energy is generated by using a resource, sunlight, which cannot be depleted. Creation of ethanol starts with photosynthesis causing a feedstock, such as sugar cane or a grain such as maize (corn), to grow. These feedstocks are processed into ethanol.

About 5% of the ethanol produced in the world in 2003 was actually a petroleum product [10]. It is made by the catalytic hydration of ethylene with sulfuric acid as the catalyst. It can also be obtained from calcium carbide, coal, oil gas, and other sources. Two million tons of petroleum-derived ethanol is produced annually. The principal suppliers are plants in the United States, Europe, and South Africa [11]. Petroleum derived ethanol (synthetic ethanol) is chemically identical to bio-ethanol and can be differentiated only by radiocarbon dating [12].

Bio-ethanol is usually obtained from the conversion of carbon based feedstock. Agricultural feedstocks are considered renewable because they get energy from the sun using photosynthesis, provided that all minerals required for growth (such as nitrogen and phosphorus) are returned to the land. Ethanol can be produced from a variety of feed stocks such as sugar cane, bagasse, miscanthus, sugar beet, sorghum, grain, switch grass, barley, hemp, kenaf, potatoes, sweet potatoes, cassava, sunflower, fruit, molasses, corn, stover, grain, wheat, straw, cotton, other biomass as well as many types of cellulose waste and harvestings The production of bio-ethanol from lignocellulosic biomass materials is shown in Figure 6.

An alternative process to produce bio-ethanol from algae is being developed by the company Algenol. Rather than grow
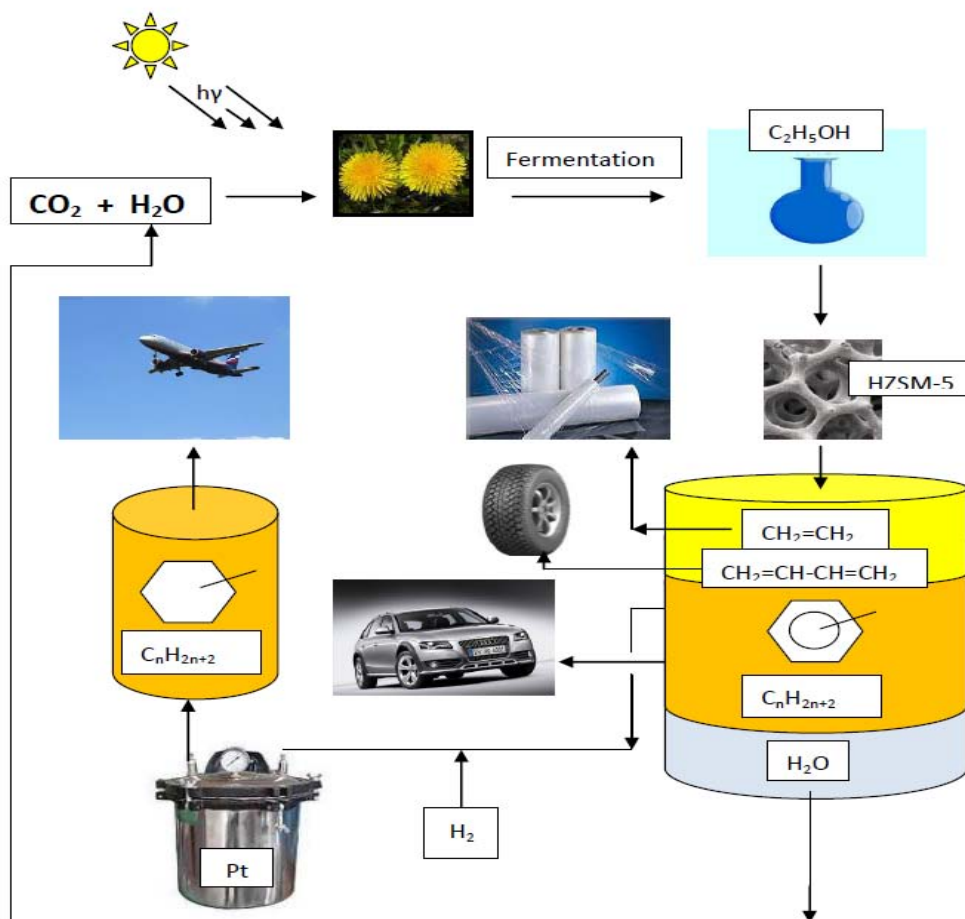

Figure 5. *Formation of bio-ethanol and its transformation to other petrochemicals.*
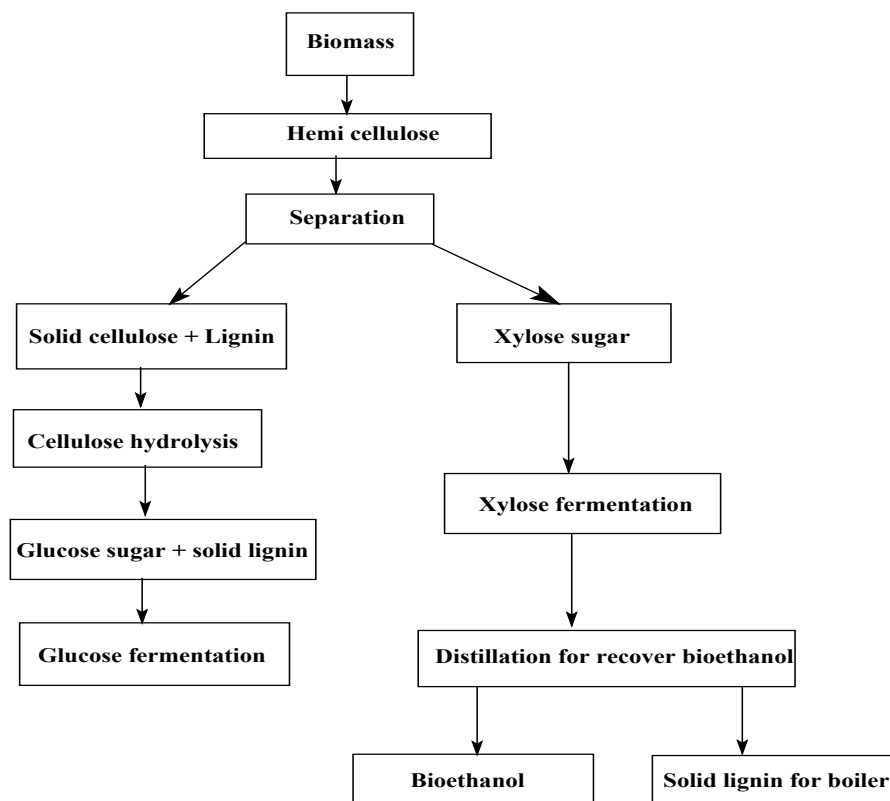
Figure 6. Flow chart for the production of bio-ethanol from lignocellulosic biomass materials [9].

algae and then harvest and ferment it, the algae grow in sunlight and produce ethanol directly which is removed without killing the algae. It is claimed the process can produce 6,000 US gallons per acre (56,000 litres per ha) per year compared with 400 US gallons per acre (3,750 l/ha) for corn production [13].

Currently, the first generation processes for the production of ethanol from corn use only a small part of the corn plant: the corn kernels are taken from the corn plant and only the starch, which represents about 50% of the dry kernel mass, is transformed into ethanol. Two types of second generation processes are under development.

The first type uses enzymes and yeast fermentation to convert the plant cellulose into ethanol while the second type uses pyrolysis to convert the whole plant to either a liquid bio-oil or a syngas. Second generation processes can also be used with plants such as grasses, wood or agricultural waste material such as straw.

The basic steps for large scale production of ethanol are: microbial (yeast) fermentation of sugars, distillation, dehydration and denaturing. Prior to fermentation, some crops require saccharification or hydrolysis of carbohydrates such as cellulose

and starch into sugars. Saccharification of cellulose is called cellulolysis. Enzymes are used to convert starch into sugar [14-16].

According to Bomgardner in [17] microbial fermentation holds promise for making renewable rubber intermediates: isoprene, iso- butane and butadiene. The compounds cover a wide swath of ground for the rubber-making industry. Five-carbon isoprene is used to make synthetic latex similar to that of rubber tree.

Two leading tire makers – Goodyear and Michelin along with Synthetic rubber manufacturer Lanxess have entered into parternership with industrial biotech firms to advance the commercial production of these rubber intermediates from sugar. They are motivated by tightening supplies of both natural and synthetic rubber, driven in recent years by strong global demand, especially from emerging economies.

In Russia, Research work is ongoing in this direction at the A. V. Tropchieva Institute of Petrochemical Synthesis in collaboration with the Moscow State University of Fine Chemical Technology named after M. V. Lomonosov and is expected to continue in the next few years.

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