

P R E F A C E

High pressure in the chemical industry is comparatively a new tool. With the discoveries of special alloys and alloy steels to withstand severe conditions of pressure, temperature, corrosion and erosion and with the introduction of new and improved high pressure accessories such as pumps and compressors, measuring and control devices it is getting more and more widespread applications in the diverse field of chemical industry.

The major use of pressure in connection with chemical reactions has been to shift the reaction equilibrium. Pressure also affects the reaction rate. The increase in concentration when a gas mixture is put under pressure tends to increase the reaction rate and results in a greater capacity of a given reactor. Pressure aids to maintain a liquid phase at elevated temperature needed to ensure economical rates, conversions and yields. Solubilities of gases in the liquid phase are also increased facilitating the reaction between a gas phase and liquid phase. Besides, pressure ensures greater degree of completion of the desired reaction, suppresses the side reactions leading to undesired products and permits the reaction to be carried out at lower temperature and thus increasing the catalyst life.

A large number of workers has been attempting to apply high pressure in the synthesis of new organic chemicals and to improve the yields of previously known reactions. The work of Ipatieff, Haber, Bergius, Fischer, Newitt, Morgan, Hardy, Reppe, Roelen, Wender, Storch, Bone, Pines and Bhattacharyya among others in this field are : outstanding. Just prior to and during the last war, extensive

researches were carried out through out the world, particularly in Germany by Rurchemie A.G. and I.G.Farbenindustrie A.G. under the able guidance of eminent chemists like Dr. O. Roelen and Dr. J.W. Reppe which resulted in the discoveries of number of completely new methods of synthesising various organic compounds of both theoretical and practical interests. Reppe's pioneering researches in this field have opened up the little known chemistry of acetylenic hydrocarbons, carbon monoxide and olefins. His work can be divided into four parts such as Vinylation, Ethynylation, polymerisation and carbonylation. Carbonylation reaction includes the synthesis of unsaturated acids and their derivatives from acetylenic hydrocarbons, carbon monoxide and water or compounds containing active hydrogen atom, saturated carboxylic acids and their derivatives from olefins, carbon monoxide and water or compounds containing active hydrogen atoms, aldehydes from olefins, carbon monoxide and hydrogen, carboxylic acids and esters from alcohols or ethers and carbon monoxide and a large number of other reactions.

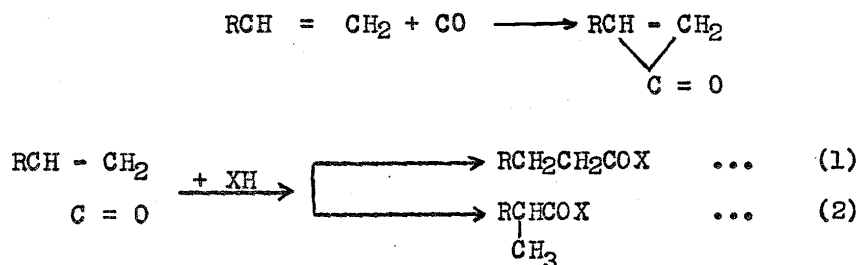
Unfortunately, most of the research and development work in this field are patented. The only available sources of information are the FIAT and BIOS reports and a few published papers. This thesis is concerned with the synthesis of methyl propionate and ethyl propionate from ethylene, carbon monoxide and methyl alcohol or ethyl alcohol under pressure and in presence of catalysts like nickel, cobalt, iron and their halides. The progress of the reactions have been studied in detail under various experimental conditions and the results which are of definite industrial significance are reported in this thesis.

CHAPTER 1

INTRODUCTION.

INTRODUCTION

Reppe's<sup>1</sup> extensive and intensive researches in the field of acetylene chemistry has opened up the general class of reactions between acetylene, carbon monoxide and compounds containing active hydrogen atom to produce unsaturated acids and their derivatives. Later he extended his work in the field of olefinic hydrocarbons<sup>2</sup>. He expected that carbon monoxide should add up to the olefinic double bonds forming the intermediate hypothetical cyclopropanone ring. This should in turn react with active hydrogen atom of hydrogen, water, alcohols, amines and mercaptans to give aldehydes, carboxylic acids, esters, amides and thioureas respectively

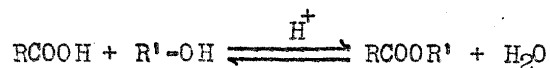


Reppe in fact could realise all the reactions which would be anticipated on account of his theory. Both straight chain (1) and branched chain(2) compounds were formed. He studied a series of both olefinic hydrocarbons and alcohols and found that the reaction was more or less general for the synthesis of organic esters. Metal carbonyls either singly or promoted with halogens particularly iodine, were used as catalysts. Although, numerous patents<sup>3-9</sup> have described the preparation of carboxylic acids from Olefins, carbon monoxide and water before Reppe discovered

these reactions, none of the previous workers attempted to synthesise carboxylic acid esters. This discovery has opened up a completely new line of approach for the synthesis of organic esters. All the ingredients needed are largely available from cheap sources of raw materials. Also, by proper choice of olefin and alcohol a wide variety of organic ester can be synthesised.

Organic esters find great industrial importance. The largest single use of ester is as solvent. The low molecular weight esters are used as solvents for lacquours, paints and varnishes. Esters are used in great amounts as extraction solvents in the isolation of naturally occuring compounds. As the low molecular weight simple esters have fruit like odours and flavours they are commercially used as the base for artificial food flavours. The higher molecular weight esters find primary uses as plasticizers. High molecular weight esters of polybasic organic acids with polyhydric alcohols known as alkyd resins are used in the preparation of coating materials. Esters of aromatic acids find extensive use as medicants.

In view of the wide application of organic esters a large number of methods have been discovered for their synthesis. The most general method is the esterification of organic acids with alcohols in presence of mineral acids as catalyst.

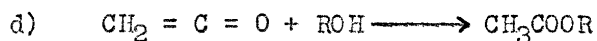
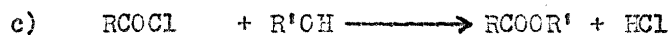
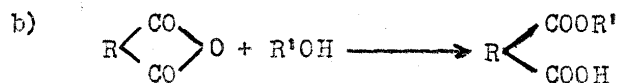
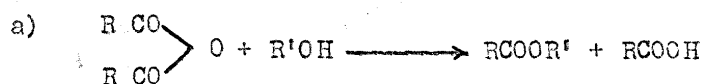


The rates and limits of esterification depend on the nature of both the acid and alcohol. The esterification reaction is a reversible

one. From industrial stand point it is desirable to push the reaction to as much completion as is economically feasible. So in the manufacturing process a high alcohol to acid ratio with the continuous removal of one of the products of reaction either water or ester is applied.

The vapour phase catalytic esterification<sup>10-12</sup> of organic acids with alcohols has received considerable attention, because the conversions obtained are generally higher than in the corresponding liquid phase process. Catalysts proposed have included silica gel, Zirconium dioxide, activated charcoal and potassium hydrogen sulfate, potassium or sodium alcoholate and difficultly reducible oxides supported on silica gel, silicon carbide and alumina.

In place of organic acids other compounds such as acid anhydrides, acyl chlorides and ketenes can also be used for esterification.



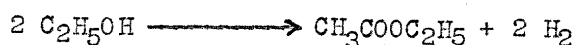
These reactions are irreversible and proceed very smoothly to completion. But as all of these compounds are rather costly

their uses industrially are restricted to few cases of synthesis of esters where more general method is not suitable.

For preparation of methyl esters, methyl halides, dimethyl sulfate and diazomethane can be used very conveniently as methylating agent.

Other routes to ester include the following:

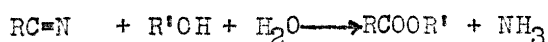
- 1) Dehydrogenation of alcohol<sup>13,14</sup> over promoted copper catalyst.



- 2) Condensation of aldehydes in presence of alkoxide catalysts<sup>15</sup>



- 3) Direct esterification of acid amides or nitriles



- 4) Action of silver salt of acid with alkyl halides



- 5) Ester - Alcohol interchange and

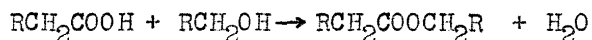
- 6) Ester - Ester interchange.

From industrial stand point, methods (1) and (2) have got immense potentiality and are being studied extensively, particularly in Russia.

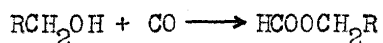
The present-day industrial method of manufacturing esters, specially the low molecular weight esters of paraffinic series is by the esterification of acids with alcohols. The success of this method depends on the cheap supply of the organic acids. Oxidation of alcohols and aldehydes and the hydrolysis of naturally occurring fats are the usual methods of synthesis of organic acids. Oxidation of petroleum hydrocarbons in the liquid phase or gas phase in fixed bed and fluidised bed<sup>16-18</sup> are recently gaining importance for the production of saturated carboxylic acids.

In view of the large availability<sup>19,20</sup> of carbon monoxide, its chemical utilisation has been the subject matter of study of different workers. These investigations have resulted in the discoveries of some completely new methods of synthesis of both carboxylic acids and esters. These may be listed as follows:

- a) The reaction of carbon monoxide with alcohols<sup>21-23</sup> to form carboxylic acids and esters under high pressure and in the presence of nickel, cobalt and iron halides catalysts.

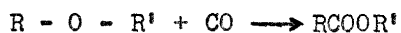


- b) Reaction of carbon monoxide with alcohols under high pressure and in presence of basic catalysts to give formates<sup>24-26</sup>

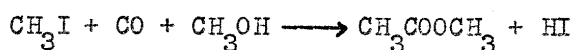




- c) Reaction of carbon monoxide with ethers to form esters and acid as the by products <sup>27-29</sup>



- d) Reaction of carbon monoxide with alkyl halides and alcohols under high pressure to give acids and esters <sup>30</sup>



And several other reactions <sup>31-33</sup> leading to the formation of dibasic acids, hydroxy acids etc.

Encouraged by the success of Reppe's work with olefins, carbon monoxide and alcohols to synthesise organic esters and in view of the availability of ethylene in large quantities in petroleum cracked gases and coke oven gas, the present investigations involving the reactions of ethylene with carbon monoxide and alcohols have been undertaken. As alcohol, ethyl and methyl alcohols have been used.

Methyl propionate and ethyl propionate are used to some extent in the preparation of artificial food flavours and in the synthetic chemical industries. Methyl propionate has got a fruity odour recalling rum. They may also be used admixed with ethyl acetate or methyl acetate as solvents. Though the industrial uses of these two esters at present are very limited, with the discovery of cheaper method of production they will be able to largely replace other esters as organic solvents. Also, establishment of the optimum conditions for these reactions and finding out the best catalyst will help to fix the general conditions that

will be required for other members of the series.

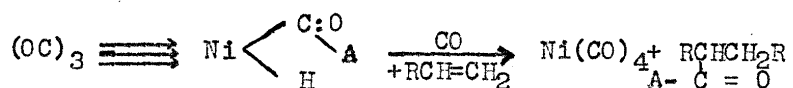
A survey of the patent literature<sup>34-51</sup> on the above synthesis have revealed that various cobalt, nickel and iron salts, either singly or promoted have been tried as the catalyst. But only the carbonyls or the salts from which carbonyls may be easily formed under the conditions of the experiments, such as halides or carboxylic acid salts have met with success. Cobalt or nickel carbonyl complexes with heavy metal salts such as

$[Co(CO)_4]_2$   $[Fe(NH_3)_6]$  have also been reported as catalysts for the reaction. In some of the more recent patents, cobalt or nickel complexes with compounds like trimethyl amine, butyl pyrrolidine, piperidine, ethyl diamine or pyrrole have been claimed to produce better results. A wide range of temperatures, pressures and residence period have been claimed to be used. The results reported in the patents are very conflicting and the formation of free acids, ethers, aldehydes, ketones and liquid hydrocarbons in addition to the desired ester have been reported.

Reppe<sup>52</sup> in his later work has discovered that carbonyls themselves are not good catalysts but the halides of the carbonyl forming metals such as cobalt, nickel and iron, particularly their iodides are most effective as catalyst. This has been further substantiated by the series of reactions studied by Bhattacharya et al.<sup>32,33,53-55</sup> Moreover, the extensive and intensive researches in this field by him and his co-workers have further revealed that the presence of small amount of water is essential for the effectiveness of these catalysts.

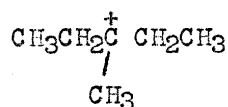
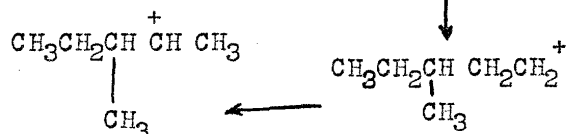
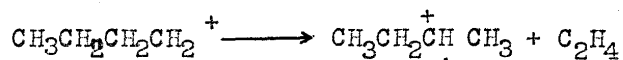
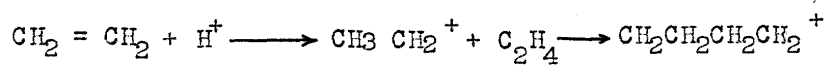
Newitt and Momen<sup>56</sup> designed experiments to obtain quantitative information about the conditions for the synthesis of organic acids, esters and amides from olefins, carbon monoxide and water, alcohols and amines respectively. Reduced nickel was used as the catalyst. With ethylene, carbon monoxide and water at 300°C and 248 atm pressure a maximum yield of 46.6% propionic acid was obtained. By using an excess of ethylene and a mixed catalyst consisting of reduced nickel, phosphoric acid and copper phosphate at 300°C and 221 atmosphere pressure they got a yield of 25% free acid and 5.4% ethyl propionate based on ethylene.

P. Piganiol and J. Vialle<sup>57</sup> used metal carbonyls as the catalyst for the reaction of olefins, carbon monoxide and compounds containing active hydrogen atom. They suggested that the metal carbonyls first combine with the reactive compounds of the type HA where A = -H, -OH, -OR, -NR<sub>2</sub> etc.



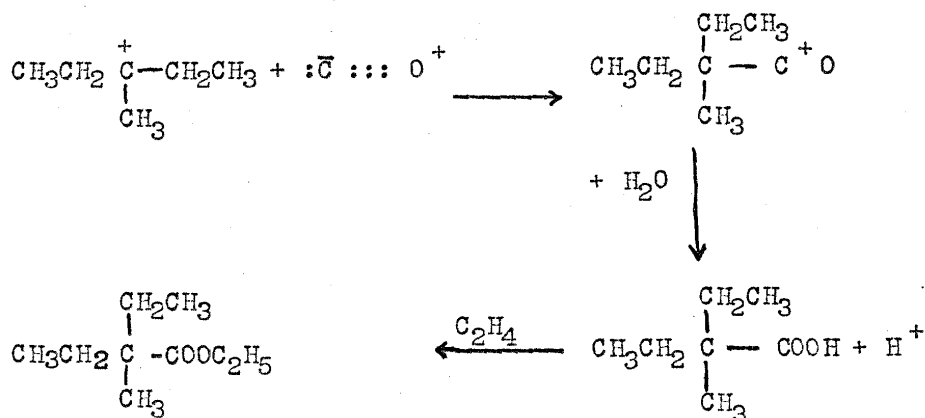
which in turn react with carbon monoxide and olefin to produce the desired compound.

By using an excess of ethylene with carbon monoxide in presence of boron trifluoride hydrate (BF<sub>3</sub> : H<sub>2</sub>O :: 1 : 1.7) catalyst quite unexpected reaction occurred leading to the formation of ethyl 2 - ethyl - 2 methyl butyrate. The authors<sup>58</sup> offered evidences of the following mechanism.



(Relatively stable carbonium ion)

This relatively stable carbonium ion can react with carbon monoxide, water and finally with  $\text{C}_2\text{H}_4$  to form the ester.



Small quantities of propionic acid was detected in the product.

G. Natta and P. Pino<sup>59</sup> in an attempt to make a comparative study on the synthesis of carboxylic acid esters from acetylene and ethylene used cobalt base catalyst. They have reported the formation of some diesters.

### RAW MATERIAL SUPPLY

The raw materials required are

- a) Ethyl alcohol
- b) Ethylene and
- c) Carbon monoxide.

The large scale industrial uses of ethanol in the wide field of chemical industries have made its methods of production highly improved. The major fraction of world's alcohol production is by the fermentation process. Alcohol can be produced from a wide variety of raw materials by the fermentation process. They may be classed as follows:

- 1) Saccharine materials containing sugar such as molasses. 'Black strap molasses' is the residue left after the extraction of crystallisable sugar and contains from 55-60% sugar. Under certain economic conditions it becomes profitable to evaporate down the original cane juice and the resulting 'high test molasses' containing as high as 78% sugar is used for alcohol production. Other saccharine materials include sugar beets, sorgo etc.

Saccharine materials have got the advantage over other types of raw materials that they need no preliminary operations and can be used directly for yeast fermentation.

- 2) Starchy materials such as (i) Cereals : Corn, grain, sorghum, oats, rye, wheat barley and rice (ii) Potatoes (iii) sweet potatoes and (iv) miscellaneous corps such as Jerusalem artichokes. High prices of cereals such as Wheat, rye, barley and rice due to their use as food stuffs restrict their use as

raw materials for alcohols with the exception of beverages. Corn is used to a considerable extent. Potatoes and sweet potatoes are also economically used. The starch content of cereals is about 50-65%. Rice contains as high as 80% starch. Potatoes contain 20% starch while sweet potatoes contain some what more nearly 30%.

The starchy materials have got to be first hydrolysed to fermentable sugars.

3) Cellulose materials: (i) Direct production of alcohol from wood entails two essential steps (a) the hydrolysis of cellulose of wood by mineral acids to simple sugar and (b) fermentation of this sugar to alcohol by yeast. Usually a ton of dry coniferous wood yields 50 gallons of 100% alcohol. Wood wastes such as chips, saw dust or cellulosic agricultural residue can also be used. (ii) From sulfite waste liquor - The waste liquor from the sulfite process of paper pulp manufacture contains from 2-3.5% sugar of which about 65% is fermentable to alcohol. About 20-22 gallons of alcohol is produced per ton of paper pulp manufactured.

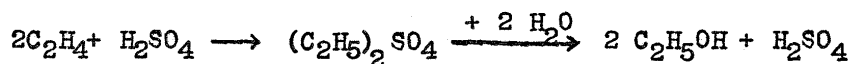
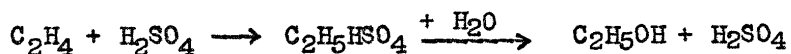
The synthetic methods of alcohol production are recently gaining importance. There are two different processes.

(1) the hydration of ethylene to ethyl alcohol<sup>60</sup>

(2) hydrogenation of carbon monoxide

The direct hydration of ethylene to ethyl alcohol is limited thermodynamically to rather low conversions<sup>61</sup>. However, the reaction can be carried out satisfactorily through ethyl sulfate. Over half

of all the alcohol consumed in the United States is made from ethylene. Usually, ethylene is first esterified with 98% sulfuric acid under pressures from 100-500 psi at a temperature of 130-170°C. It is later hydrolysed with measured quantity of water. Some ether is also formed though the conditions are usually chosen to minimise ether formation.



In order to avoid reconcentration of acid, hydration of ethylene have been tried with dilute sulfuric acid where sulfuric acid in effect acts as a catalyst.

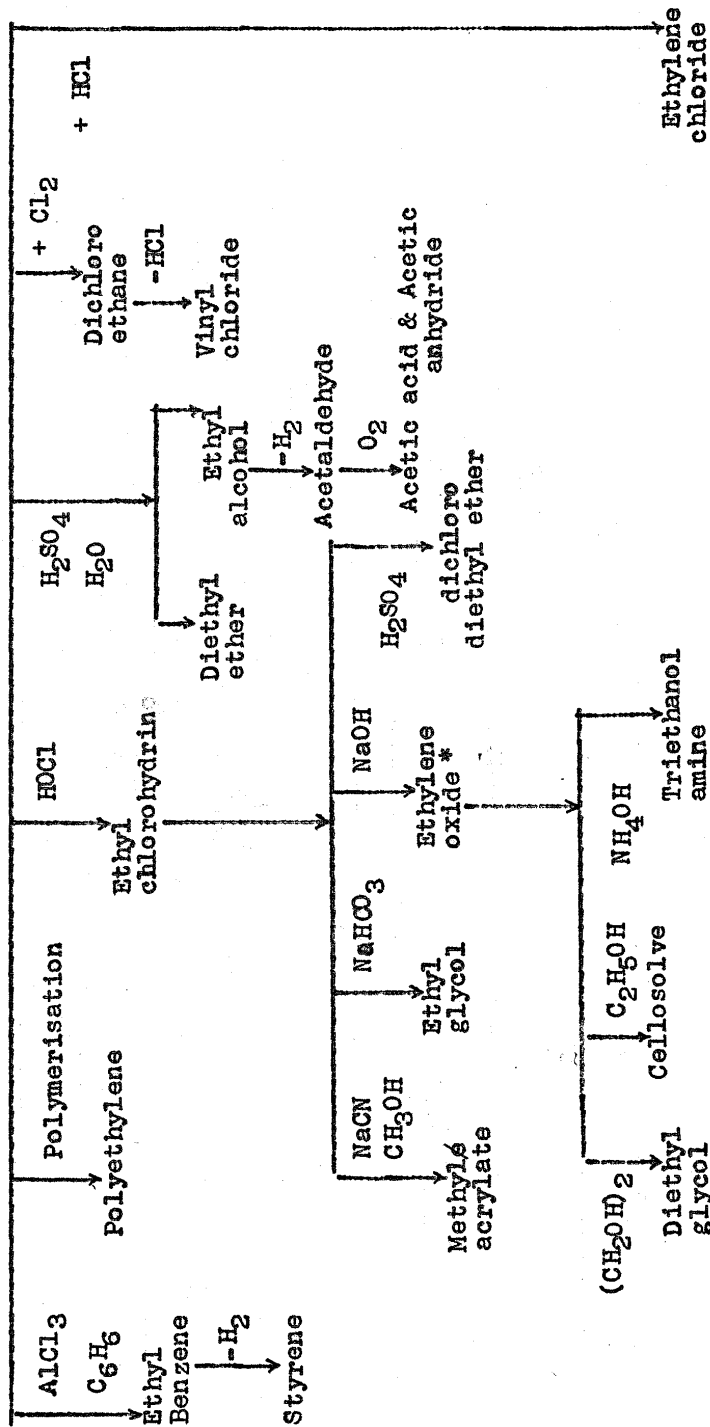
2) A potential important source of ethanol is the 'synthine' or 'synthol' process using natural gas as raw material<sup>62-65</sup>.

Ethylene: The large scale availability of ethylene has made it the starting material for the production of large number of industrially important organic chemicals. Various organic chemicals that can be obtained from ethylene are summarised in table 1.

Coke oven gas contain about 2-3.5% ethylene. Pyrolysis of petroleum fractions provide large amount of ethylene. The concentration of ethylene in the cracked gas may be as high as 30-40%. Cracking of heavier petroleum fractions yields large amount of ethylene as by-product. Recovery of ethylene and its

TABLE - 1

PRODUCTS FROM ETHYLENE



\* May also be produced by the direct oxidation of ethylene.

Ethylene also finds application as refrigerent, in producing cutting flames in welding processes, as an anesthetic and as an accelerator for plant growth and fruit ripening.



purification from the cracked gases is the most important part of ethylene manufacture. The following methods are employed.

- 1) Low temperature low pressure straight fractionation
- 2) Low temperature high pressure straight fractionation
- 3) Low temperature absorption and fractionation
- 4) Hypersorption and
- 5) Solvent extraction

In countries where petroleum supply is limited, ethylene can be manufactured by the hydrogenation of acetylene obtained by the action of water on calcium carbide, dehydration of alcohol or ether or by the controlled hydrogenation of carbon monoxide.<sup>66</sup>

#### Carbon monoxide

Carbon monoxide has for many years been of great interest to chemical industry because of its ability to participate in a wide variety of reactions. The various industrially important products from carbon monoxide are summarised in table 2.

The potential availability of carbon monoxide as a cheap material for chemical synthesis is enormous. For industrial purposes coal, coke and naturally occurring hydrocarbons like petroleum and natural gas are the primary sources of carbon monoxide. Perhaps the largest source of carbon monoxide is to be found in the gases made from coal and coke by blue water gas generators, producers, blast furnaces and coke ovens. The proportion of carbon monoxide content of the above gases are given below<sup>67</sup>.

	<u>Blue water gas</u>	<u>Producer gas</u>	<u>Blast furnace gas</u>	<u>Coke oven gas</u>
CO (% by Vol.)	37.8 to 42.8	22 - 26	26.2 to 27.3	5.0 to 6.8

Blue water gas contains the highest percentage of carbon monoxide and is most frequently employed. Even higher proportions of carbon monoxide may be obtained by blowing carbon dioxide instead of steam over hot coke in a water gas set. In areas producing natural gas carbon monoxide may be produced by reacting the hydrocarbon gases with oxygen, air, steam or carbondioxide. Various by-product gases also contain carbon monoxide in sufficient concentrations to be used on a limited scale.

TABLE - 2

PRODUCTS OF INDUSTRIAL IMPORTANCE FROM CARBON MONOXIDE & HYDROGEN

Process	Catalysts	Promoters	Pressure atm.	Temperature (°C)	Products
Fischer Tropsch synthesis.	Iron, Cobalt, Nickel Ru	ThO <sub>2</sub> , MgO, Al <sub>2</sub> O <sub>3</sub> , K <sub>2</sub> O -	1 - 30 100-1000	150 - 350 150- 250	Paraffinic and olefinic hydrocarbons and large quantity of oxygenated products.
Methanol synthesis.	ZnO, Cu, MnO, Cr <sub>2</sub> O <sub>3</sub>	-	100 to 1000	200 to 400	Methanol.
Higher Alcohol Synthesis.	ZnO, Cu, MnO, Cr <sub>2</sub> O <sub>3</sub>	alkali	100 - 400	300 to 450	Methanol and higher alcohols.
Iso Synthesis.	ThO <sub>2</sub> , ZrO, Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	100 to 1000	400 to 500	Saturated branched hydrocarbons.