

C₁ Chemistry: potential and developments

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Abstract - C₁ chemistry based on synthesis gas, methane and carbon dioxide offers many routes to industrial chemicals. The synthesis gas chemistry can be classified into a direct and indirect approach. The present economic climate favours direct routes of CO hydrogenation which retain at least one of the oxygen atoms of the original CO reactant. Potential applications exist for alcohols, acids, anhydrides and esters. Methanol can be considered to be a potential building block representing the indirect conversion route. Based on methanol the synthesis of a variety of chemicals such as acetic acid, ethanol, ethylene glycol, acetaldehyde and many more is feasible. The second part deals with applications of methane in C₁ chemistry. Principally, two approaches are feasible: methane as feedstock for synthesis gas/methanol and coupling of methane to C_n' products. Finally in the last part potential reactions to utilize CO₂ as building block for chemicals will be discussed.

INTRODUCTION

Recent concern over availability and costs of petroleum feedstocks has given rise to a growing interest in alternative carbon sources such as natural gas, coal, biomass, shale oil and tar sands. One potential development is the gasification of all these resources into synthesis gas and its use as a common feedstock for the chemical industry. Such a development would parallel the history of utilizing the myriad number of compounds present in crude oil by having developed routes in the past in which oil is converted to the unifying building blocks ethene, propene, butadiene, benzene and xylenes. More than 90 % of all industrial chemicals originate from these five crude oil derivatives.

Synthesis gas also forms the basis of C₁ chemistry. Under C₁ chemistry in a broad sense the formation of multicarbon molecules from single-carbon feedstocks is understood. Frequently, however, only the loosely defined body of chemistry and technology contained in the area of synthesis gas based developments is referred to as C₁ chemistry as is shown in Fig. 1.

Although in the short term crude oil seems in plentiful supply, it should be remembered that, based on existing knowledge, the estimated reserves of crude oil are limited and long range synthesis gas will compete with mineral oil and the basic research and development for its future application must be done today to have it available when it is needed.

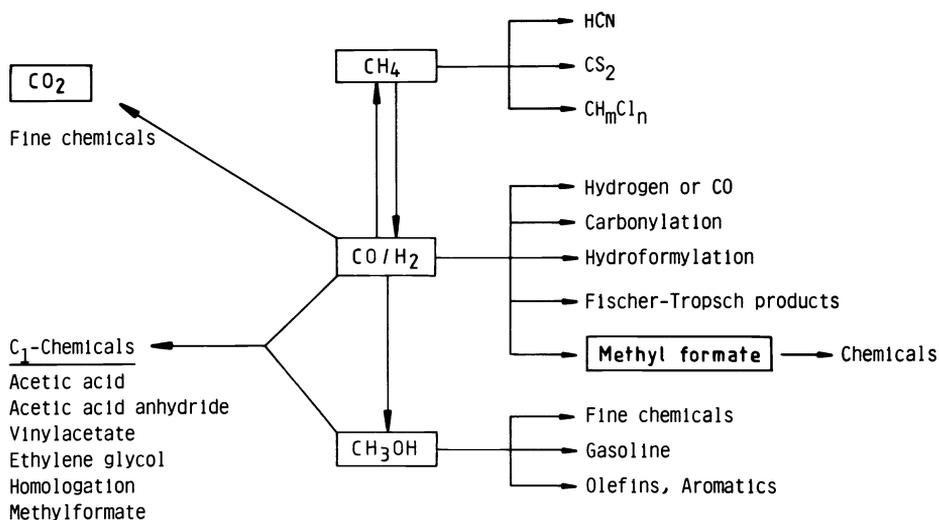


Fig. 1. C₁ Building blocks

Opportunities for C₁ chemistry can also be seen considering the following arguments:

Availability of own carbon resources: Countries with huge own carbon resources such as coal, natural gas or biomass may find it beneficial for political or financial reasons to develop their own resources.

Innovation: The chances in searching for a competitive advantage are greater where new technology exists. Using crude oil derivatives narrows the opportunities for new processes. Similar technological paths exist for all competitors.

Independence: An erratic behaviour of feedstock prices and a shortage in availability makes planning and forecasting very difficult. A reliable, secure feedstock supply and long term contracts at calculable prices are the basis of a prosperous industry. Independence also embraces concern for national security aimed at using own available feedstocks.

Environmental constraints: In our today's world, environmental considerations have developed into an important factor. Processes, which burden the environment, will be phased out.

However, the most critical factor determining the size and the speed of the development of C₁ chemistry will be the price of crude oil. Low prices will push major developments in this area into the distant future.

It is also reasonable to assume that prior to the exclusive use of chemicals, derived from feedstocks other than mineral oil, chemicals based on crude oil and chemicals originating from alternate feedstocks will supplement each other. This situation has already arisen. For instance, in Germany, Hoechst uses coal derived CO/H₂ to hydroformylate olefins, which stem from crude oil. In the following, special attention will be focused on C₁ chemistry based on synthesis gas, methane and carbon dioxide.

1 C₁ CHEMISTRY BASED ON SYNTHESIS GAS

Synthesis gas offers many routes to industrial chemicals. They can be classified in a direct and indirect path. The direct path involves methanation, Fischer-Tropsch chemistry and synthesis of oxygenates. The indirect path embraces carbonylation, methanol and methyl formate chemistry. Table 1 lists a variety of practiced or high potential CO hydrogenation reactions.

TABLE 1. Hydrogenation of CO

		ratio	loss (%)	
		CO:H ₂	as H ₂ O	
<u>Direct conversion</u>				
CO + 2 H ₂	→	methanol	1:2	-
2 CO + 2 H ₂	→	acetic acid	1:1	-
2 CO + 2 H ₂	→	methyl formate	1:1	-
2 CO + 4 H ₂	→	ethanol	1:2	28
3 CO + 6 H ₂	→	propanol	1:2	38
2 CO + 3 H ₂	→	ethylene glycol	2:3	-
4 CO + 8 H ₂	→	iso butanol	1:2	50
2 CO + 4 H ₂	→	ethylene	1:2	56
16 CO + 33 H ₂	→	n-hexadecane ^{a)}	1:2.1	56
<u>Indirect conversion</u>				
CH ₃ OH + CO	→	acetic acid	-	-
CH ₃ COOCH ₃ + CO	→	acetic anhydride	-	-
CH ₃ OH	→	ethylene	-	56

a) representative for Fischer-Tropsch

Two facts are obvious from Table 1: a) the ratio of CO:H₂ needed is different b) various amounts of water are produced. The molecular loss becomes even worse when CO₂ is formed besides of water. Both the ratio of CO:H₂ and the formation of water affect the economics of CO/H₂ technology significantly.

Direct CO/H₂ conversion (ref. 1-3): The direct conversion deals with the straight hydrogenation of carbon monoxide to paraffins, olefins and oxygen containing products. Best known in the direct CO hydrogenation is the Fischer-Tropsch synthesis yielding mixtures of mainly linear alkanes and/or alkenes. Mechanistically it can be described as a reductive oligomerization of carbon monoxide following a geometric progression (Schulz-Flory distribution). With α -values close to one broad product distributions are obtained, whereas small α -values predominantly yield methane. Therefore, prior to entering a costly research and development program a simple calculation may help to evaluate whether the mathematically determined product distribution can be balanced on the market.

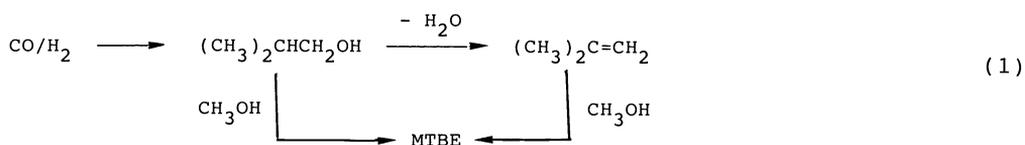
Shortly after the oil crisis many efforts were seen to convert CO/H₂ to methane (SNG). As a consequence of the increased search for oil vast amounts of natural gas were discovered making SNG in most instances to an obsolete target.

Some interest still centers around Fischer-Tropsch as it is practiced at Sasol in South Africa. However, tailoring (selectivity) of the product distribution remains a challenging goal attacked in many research labora-

tories. Some encouraging results for olefins have been reported, which up to date are of only academic interest (ref. 4). Shell recently has released details of its new process to transform natural gas to middle distillates, such as naphtha, gasoil and kerosene. In this scheme, CH_4 is first converted to CO/H_2 followed by a Fischer-Tropsch type reaction using a proprietary catalyst. To tailor the product slate the paraffins are hydrocracked to produce middle distillate (ref. 5).

Based on economics (see Table 1) the formation of oxygenates is favoured. Methanol is by far the most promising chemical manufactured already in many millions of tons. The higher alcohols such as ethanol and propanol are potential candidates for gasoline usage, alone or blended. IFP has reported catalysts, which synthesize a spectrum of alcohols (50-70 % methanol, 16-23 % ethanol, propanol, 4-7 % n-butanol, 2-3 % pentanol, 1-3 % C_6+ alcohols), a process which IFP currently develops together with Idemitsu in Japan (ref. 6). Also from Japan comes the message, that ethanol is being produced from syngas in a bench-scale unit by Kyowa Yuka. The vapor-phase process uses a supported rhodium catalyst and the production of 200 g/h of ethanol per g of catalyst is claimed (ref. 7).

In this connection the reduction of acetic acid to ethanol developed by Humphreys & Glasgow in conjunction with BASF/Monsanto must be mentioned as an attractive route to fuel alcohol or ethanol/ethene respectively. Of potential interest is also the direct CO hydrogenation to isobutanol, which can be dehydrated to isobutene (chemical usage) or converted with methanol to MTBE (eq. 1).



This process was practiced up to 1952 by BASF and is still used in the German Democratic Republic. In our laboratory, we could increase the share of isobutanol up to 25 % (BASF plant 11 %) at 176 g/l h (ref. 8).

Most remarkable is the high-pressure, rhodium catalyzed homogeneous reduction of CO pioneered by Union Carbide aimed at an industrial synthesis of ethylene glycol (ref. 3, 9). As is evident from Table 1, this reaction proceeds without a loss via formation of water or CO_2 . Furthermore the great technical potential of this process is also obvious when considering the poor selectivity with which ethylene glycol is currently manufactured from ethene. From a technical point of view, however, the rhodium catalyzed synthesis of ethylene glycol possesses various disadvantages: First of all the high pressure being necessary for reasonable activities and selectivities has to be quoted. A very expensive metal, rhodium, is used. Catalyst recycle and circumvention of any rhodium loss will be difficult. To manufacture fibre grade ethylene glycol the purification costs will be high. Various attempts are known to use a less costly metal and/or to lower the pressure, but a breakthrough has not been reported, so far.

TABLE 2. Chemicals from methanol

<u>Carbonylation</u>		<u>Reductive carbonylation</u>	
CH ₃ OH	$\xrightarrow{\text{CO}}$	acetic acid (Monsanto)	
CH ₃ OH	$\xrightarrow{\text{CO}}$	methyl formate	
CH ₃ OH	$\xrightarrow{\text{CO}}$	methyl acetate	
methyl acetate	$\xrightarrow{\text{CO}}$	acetic anhydride (Tennessee Eastman)	
formaldehyde	\longrightarrow	ethylene glycol	
<u>Oxidative carbonylation</u>		<u>Others</u>	
CH ₃ OH	$\xrightarrow{\text{CO/O}_2}$	dimethyl carbonate	
CH ₃ OH	$\xrightarrow{\text{CO/O}_2 \text{ or NO}}$	dimethyl oxalate \longrightarrow ethylene glycol	
CH ₃ OH	\longrightarrow	olefins (Mobil)	
CH ₃ OH	\longrightarrow	CO/H ₂ \longrightarrow	pure CO or H ₂
CH ₃ OH	$\xrightarrow{\text{toluene}}$	styrene	

The great desire for a CO based new ethylene glycol synthesis is also underlined by the research efforts being reported by various companies (see Table 2). Besides the direct hydrogenation also routes via methanol or formaldehyde are under investigation. For many years Du Pont practiced a formaldehyde based process which involved hydrogenation of the ester of glycolic acid. The critical step, which led to the plant's final shut down, was the hydrogenation of the glycolic acid. Lately, formaldehyde has again gained interest. The reductive carbonylation of formaldehyde yields glycol dialdehyde, which can be hydrogenated to ethylene glycol. Various companies are working on the oxidative carbonylation of methanol to dimethyl oxalate, which also could be hydrogenated to glycol (Union Carbide, Ube Industries).

A target of interest can also be seen in the direct hydrogenation of CO to acetic acid. It remains to be seen, whether this path ever can compete with the indirect one, the Monsanto process, which is so efficient.

Indirect CO/H₂ conversion: Among organic chemicals, methanol belongs to industry's most dynamic and potential products amounting to about 16 million t in 1986. In addition to the traditional market a very significant demand for methanol in new areas such as energy or single cell protein may emerge in the future. If energy prices develop in such a way that it becomes economically attractive to use methanol in gasoline or as a fuel for power production, the market potential in these areas is almost unlimited. This development, however, will be governed by political decisions and so far predictions for the future are almost impossible. The chemical industry has always been tied very closely to the usage and development of energy whether it was coal or crude oil. Also in the future the fate of the chemical industry

will be connected to the fate of the energy resources. If methanol should ever enter into the energy field, it will be available as feedstock for the chemical industry in practically any amount and at rather low cost. Therefore, a methanol based chemistry appears very attractive.

Three types of reactions based on methanol, which are shown in Table 2, can be distinguished: Carbonylation, reductive carbonylation and oxidative carbonylation.

The carbonylation of methanol is the best process to manufacture acetic acid. Based on methyl acetate, the reaction product of methanol and acetic acid, acetic anhydride is industrially synthesized via carbonylation by Tennessee Eastman. It is noteworthy that this process is based on coal derived synthesis gas to give as final product cellulose acetate. A combination of Monsanto and Tennessee Eastman technology opens the door for the combined synthesis of acetic acid and/or acetic anhydride.

While the direct carbonylation is well accepted by industry, the reductive and oxidative carbonylation is still in the research and development stage. Routes to propionic acid are announced by Texaco (ref. 10). Based on methylacetate Halcon has also claimed a process for the reductive carbonylation to ethylidene diacetate, which can be converted to vinylacetate. It must be seen whether this route, in which the vinyl group amounts to only 28 % in the molecule, will ever displace the Wacker-Hoechst process. Methylacetate can be reductively carbonylated to ethyl acetate, which upon pyrolysis gives ethene, another approach to synthesize ethene from methanol (ref. 11). In this connection the Mobil process must be quoted, which paved the way to various potential routes for olefins based on methanol.

Quite promising looks the reductive carbonylation of methanol (homologation) to yield ethanol or acetaldehyde. Especially the variant acetaldehyde looks enticing from a technical point of view. At conversions up to 97 % selectivities up to 80 % could be obtained (ref. 8).

Finally, methyl formate must be mentioned as a potential C_1 intermediate (ref. 12). It can be synthesized directly from CO/H_2 or indirectly via methanol. Around methyl formate various potential applications could revolve as is shown in Fig. 2.

A substantial research and development effort in C_1 chemistry is carried out in Japan within a National Research and Development Program sponsored by MITI. Among 14 companies four goals have been set up: ethylene glycol, ethanol, acetic acid and olefins. According to private communications all four groups have met their targets, and it will be interesting, to see their results being published.

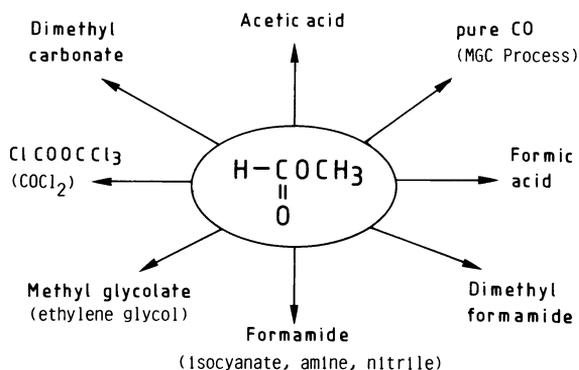


Fig. 2. Methyl formate as intermediate in C_1 chemistry

2 C₁ CHEMISTRY BASED ON METHANE (REF. 13)

Methane constitutes one of the most abundant carbon resources of the world. Besides for energy, methane is used already to produce a number of C₁ chemicals (CH₃OH, C_X_n, HCN). Also its technical dimerization to acetylene is known. Recently, considerable interest emerged to couple methane to substitute ethene or to use it directly as feedstock for the synthesis of chemicals. The thermodynamic behaviour and the heat of reaction problem represent a barrier one must be aware of. A variety of approaches have been reported, which are listed in Table 3.

TABLE 3. Activation of methane

CH ₄	→	C ₂ 's products (oxidative coupling)
CH ₄	$\xrightarrow{\text{O}_2, \text{C}_1\text{-C}_4 \text{ alkanes}}$	olefins (oxidative methylation)
CH ₄	$\xrightarrow{\text{CH}_3\text{CN}, \text{O}_2}$	acrylonitrile
CH ₄	→	olefins (Benson process)
CH ₄	$\xrightarrow{\text{Cl}_2}$	vinyl chloride (Benson process)
CH ₄	$\xrightarrow{\text{O}_2}$	methanol/formaldehyde

So far, selectivities and activities in most reactions are poor. There is a great need to develop better catalysts.

Recent remarkable examples of alkane activation in homogeneous systems under mild conditions have given rise to great enthusiasm (ref. 14). However, it must be emphasized that these results in the majority of cases are stoichiometric and, so far, are of mainly academic interest, but they may pave the way to a better understanding on which future applications could rest.

In summary, long range two approaches are feasible to use methane: a) conversion to synthesis gas/methanol, b) coupling to C₂'s products. Whereas the first technically is well established, the second needs much further research and development work.

3 C₁ CHEMISTRY BASED ON CARBON DIOXIDE (REF. 15)

The total amount of carbon dioxide in the atmosphere and in the oceans is estimated at 10¹⁴ t, a staggering amount when considering its potential as a building block for chemicals. For a long time CO₂ is used by industry to manufacture chemicals such as urea, ethylene carbonate and salicylic acid. It also has been known for a long time that CO₂ can be reduced by hydrogen yielding methanol as practiced in the process to manufacture methanol, one of the biggest applications of CO₂ usage in the chemical industry. Thermodynamically CO₂ is not favoured for chemical reactions, and a parallel to H₂O chemistry may be seen here.

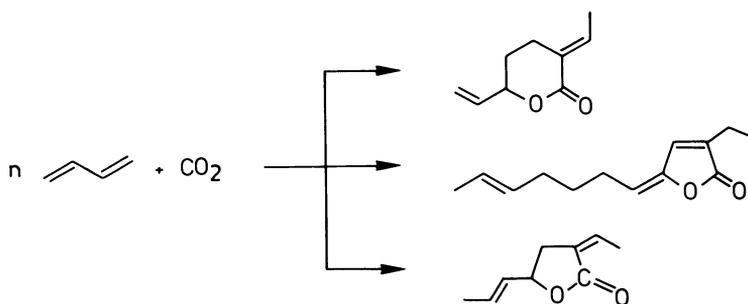


Fig. 3. Reactions of butadiene with CO_2

Lately CO_2 has attracted the interest of coordination chemists and many complexes and reactions with CO_2 are known. Especially fruitful are catalytic reactions of CO_2 with alkynes and diolefins, which proceed with high selectivities at reasonable conversions, exemplified in Fig. 3 for butadiene.

SUMMARY

There are many opportunities for C_1 chemistry based on synthesis gas, methane activation and carbon dioxide. Fuel applications as well as the production of large volume and fine chemical syntheses can be based on these feedstocks. More research and development work, however, is needed to introduce some of the many leads into practice.

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