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# Natural gas chemical transformations: The path to refining in the future

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## Abstract

Environmental problems caused by both mobile and fixed sources, such as vehicles and chemical plants, are drastically changing the main objectives of the refining industry, as cleaner sulfur-free fuels are obligatory. Therefore, the search for alternative hydrocarbon sources, which enable the traditional refiner to reduce contaminants without major investments, is very important. This paper presents the possibilities of using natural gas as a clean raw material to replace oil. The main options of catalytic chemical transformations are discussed. Gas-to-gas (GTG) transformations, yielding dimethyl ether or olefins, as well as gas-to-liquid (GTL) processes, generating medium distillates, paraffin and naphtha, or even aromatics via a different route, are discussed. Finally, the challenges in terms of the future of catalysis are also presented.

*Keywords:* Dimethyl ether; Gas-to-liquid processes; Natural gas; Olefins

## 1. Introduction

Environmental demands for even cleaner fuels, which require them to be sulfur-free, to contain a minimum of aromatics and to generate a minimum of nitrogen oxides, soot and non-reacting hydrocarbons are modifying the traditional objectives of the refining industry in a drastic manner. For many years, this industry stood out for its search to increase conversion and selectivity of gasoline and medium distillate products, principally when heavy oils, which had an inconvenient API grade and low reactivity for the creation of high quality products, were used as a raw material. The environmental worries were of secondary importance at that time.

The new environmental regulations obliged the refiners to review their objectives. Although possible to reduce contaminants such as sulfur, nitrogen and aromatic compounds by introducing a new oil or derivatives hydrotreatment unit, such units require a lot of energy and considerably reduce the refinery's energy efficiency, without mentioning the high cost of installation (CAPEX) and operation (OPEX). It is estimated that the CAPEX of a new refinery, which traditionally would be between 12,000 and 14,000 per barrel per day, depending on the degree of sophistication required, rises vertically to US$ 18,000–20,000 per barrel when hydrotreatment units are necessary. Furthermore, because of their high-energy consumption, it is very possible that an improvement in air quality will be at the cost of an increase to the greenhouse effect, due to the emissions that occur during the production of this same diesel. Therefore, the search for alternative raw materials, such as natural gas and biomass material, is becoming an obligation.

Among the potentially interesting raw materials, natural gas appears to be the most promising. It is hoped that the energy model currently used in the world, in which oil predominates, will undergo considerable modifications, with the contribution of natural gas becoming ever greater. However, a hybrid model, in which the two sources coexist, will be the best transitory solution for the future economy, totally based on hydrogen. This model allows for the chemical transformation of natural gas into derivatives, similar to those obtained from oil (diesel, gasoline, petrochemical naphtha), thereby making the sale of natural

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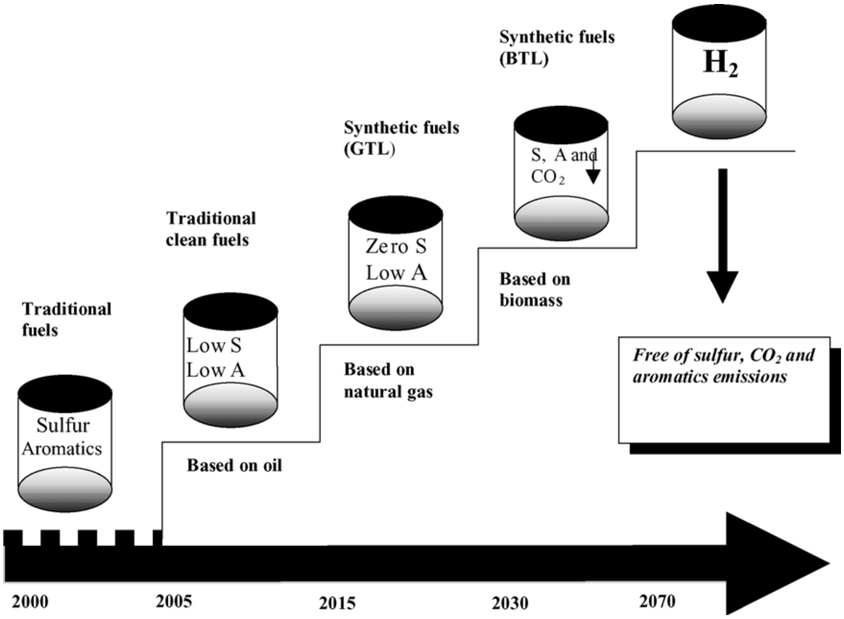

Fig. 1. Fuel technological trajectory and future forecast.

gas easier in a recognized commodities market. The chart of Fig. 1 shows, in accordance with this new model, the technological trajectory of the fuels.

Taking into account that the principal component of natural gas is methane, a considerably inert molecule and with generally very low reactivity, it is hoped that much will still be done in the field of C1 chemistry, to enable the successful implementation of the hybrid model mentioned above. It is unnecessary to mention that the C1 routes are traditionally catalytic. Hence, what is called *refining in the future* will develop the interest in general catalysis and new catalysts, or even innovative applications of traditional catalytic materials.

Three areas are clearly extremely promising, when natural gas is the main raw material. The first is the transformation of natural gas (or any raw material rich in methane, such as biogas or gasified biomass) into synthesis gas ($CO + H_2$), by a steam reforming process, autothermal reforming or partial oxidation. The synthesis gas undergoes a Fischer–Tropsch reaction, forming hydrocarbons in the diesel and petrochemical naphtha range, in a route known as traditional gas-to-liquid (GTL), as it transforms gas into liquid derivatives. The second is the transformation of natural gas into synthesis gas, as in the previous example, but this, however, reacts to form other gases, of which dimethyl ether is, undoubtedly, the most important. These routes, known as gas-to-gas (GTG), have a very elegant alternative, which consists of the activation of the methane by halogenation, forming halomethanes, which can further react to yield dimethyl ether or olefins. Finally, much effort has to be made to develop a catalyst, which allows direct synthesis of high molecular weight hydrocarbons from methane. This route would avoid the installation of a synthesis gas production unit, which still represents the major part of the costs of a traditional GTL process. For catalysis, all three options present considerable challenges, which shall be discussed next.

## 2. GTG processes

### 2.1. Dimethyl ether (DME)

Dimethyl ether is the simplest of the ethers. Currently, this substance has been used in aerosol sprays for painting, cosmetics and agriculture, substituting chlorine and fluorine-based compounds, which are harmful to the environment [1].

Recently, DME has come to the attention of various companies, research centers and universities in leading countries, due to its potential for use as a fuel [2–6]. In fact, this substance can be used in diesel powered engines, thermoelectric power plants and fuel cells, as well as a substitute for liquefied petroleum gas (LPG). The fact that DME is obtained from natural gas should also be highlighted, which allows production costs to be independent of the swings in the price of oil, as well as the wide availability of the raw material, bearing in mind the current world reserves of this gas. All of these facts together make DME known currently as the '*Fuel Of The XXI Century*'.

Various recent studies undertaken in Japan, the USA and Korea, among other countries [7–10], irrefutably showed the technical viability of the use of DME in diesel-powered engines. In fact, DME has a very high cetane index (60), it does not emit particles or sulfur oxides upon burning, making it one of the best fuels in respect to the pollution

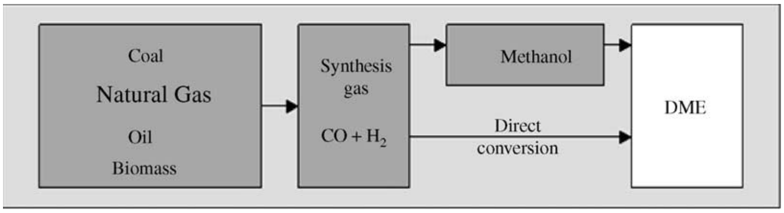

Fig. 2. Dimethyl ether production routes.

issue [5]. However, recent information obtained from long duration engine tests showed that some development still needs to be carried out. In this context, the following is highlighted: the need for the development of low cost elastomers, as DME may attack traditional polymers, additives seeking to alter the properties of lubricants and the viscosity of the DME and injection pumps specifically for DME [7–10].

DME is colorless, its boiling point is −25.1 °C and it has properties similar to propane and butane, the principal constituents of LPG. As it is easily liquefied, it can be distributed and stored employing the same technology as used for LPG. These properties allow its use as a substitute for liquefied petroleum gas, despite having a net heating value (6900 kcal/kg) slightly lower than the oil derivatives previously mentioned. Recently, disclosed technical–economical evaluation work indicates that DME production costs are competitive with those for LPG on the international market. It was also shown that modifications to ovens and containers are not very relevant [11].

As shown in Fig. 2, DME can be produced in two distinct ways: the first called the indirect route produces methanol, then promoting its dehydration; the second, known as the direct route, produces DME in a single stage, using bi-functional catalysts.

Although synthesis from methanol is simpler, direct synthesis is more interesting as far as catalysis is concerned, and it may also become more attractive economically. The principal reactions involved in DME direct synthesis are as follows:

$$2CO + 4H_2 \leftrightarrow 2CH_3OH \quad (1)$$

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \quad (2)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (3)$$

It is evident that methanol is the main intermediary in direct synthesis and that the water displacement reaction is a strong competitor to the principal reaction. The catalysts must be bi-functional, having methanol synthesis characteristic metallic sites, yet containing sufficient acidity for its dehydration reaction to occur. They must also be capable of promoting the $CO_2$ formation reaction, which becomes ever more significant as water is being generated by the dehydration stage.

Fig. 3 shows data from bi-functional catalysts, where it is clear what influence the acid and metallic sites have on the selectivity of the process. Greater acidity favors the formation of DME, while an increase in the concentration of metallic sites promotes conversion to methanol. The formation of $CO_2$ follows that of DME, as a clear indication that water generated by the dehydration continues to react with CO.

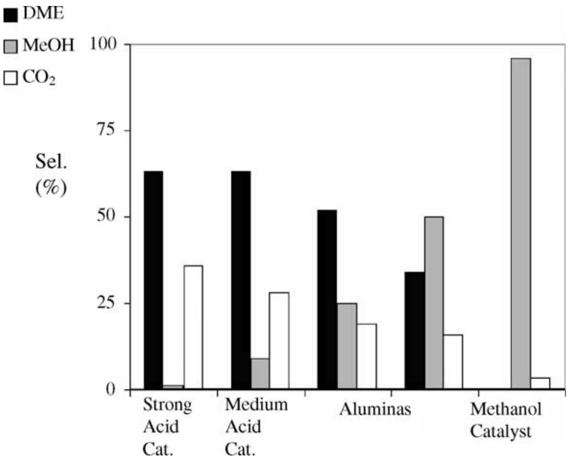

Fig. 3. Influence of the catalyst composition (concentration of acid sites vs. metallic sites) in the formation of DME by direct synthesis.

Therefore, direct synthesis has some interesting challenges in the development of catalysts. Among these, one can mention preparation methods that allow the introduction of classic metallic sites for methanol synthesis (Cu, Zn) without blocking acid sites, presuming that these may be in zeolite cavities, or the introduction of acid sites in a hydrotalcite Cu/Zn/Al, recognized as the best catalyst for methanol synthesis. Equally interesting is the search for a system that catalyses $CO_2$ hydrogenation to methanol, thereby closing the cycle shown in the reactions (1)–(3).

## 3. Production of olefins (GTO)

UOP recently proposed a very interesting route for the production of light olefins (ethene, propene) from methanol (better known as the MTO, methanol-to-olefins, process) [12]. This process uses a silico–alumino-phosphate (SAPO-34) as a catalyst, which represents a new commercial use for a structure similar to the zeolites. Fig. 4 shows this route in comparison to the existing ones. For methanol synthesis, new catalytic systems are bringing interest to this already well-known synthesis. The use of Fe and Cu phthalocyanine complexes, encapsulated in zeolites was found to be able to

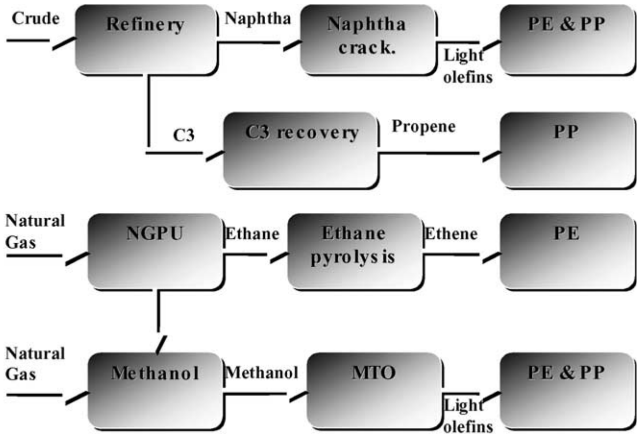

Fig. 4. Polyolefin production routes from different raw materials.

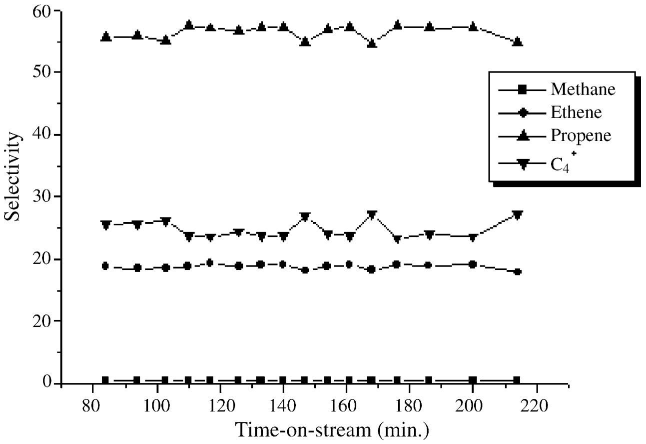

Fig. 5. Formation of light olefins from halogenated methane derivatives.

convert methane into a mixture of methanol and formaldehyde with high conversion [13].

An interesting field of research in the C1 chemistry area is the activation of methane by halogenation, in a manner to avoid the high costs of the reforming stage, which still represents the most expensive part of the GTO process. The halogenation reaction is exothermic, while the methane reforming is highly endothermic. For example, the methane chlorination reaction releases 23 kcal/mol, while the methane reforming with water consumes 49 kcal/mol. Therefore, the heat released during chlorination could be utilized in subsequent stages of the process, improving the thermal balance of this new route. The reactions involved are the following:

$$CH_4 + Cl_2 \leftrightarrow CH_3Cl + HCl \tag{4}$$

$$2CH_3Cl \leftrightarrow CH_3{=}CH_3 + HCl \tag{5}$$

$$HCl + O_2 \leftrightarrow Cl_2 + H_2O \tag{6}$$

The hydrochloric acid reoxidation, regenerating the chlorine, should also be taken into account, as shown in reaction (6). Catalysts for this type of process are being studied, and metal-containing zeolites appear to be very promising [14,15]. Fig. 5 shows the results of selectivity for the halomethane reaction with a metal-containing zeolite. Note the considerable formation of propene and ethene, which is a good indication of this route's technical viability.

## 4. GTL processes

### 4.1. Traditional GTL

GTL technology is based on the conversion of natural gas to liquid fuels in three stages: synthesis gas generation, production of heavy-chain hydrocarbons by Fischer–Tropsch synthesis and heavy fraction hydrocracking for production of useful compounds such as naphtha, diesel and lubricants (Fig. 6). The synthesis gas generation stage corresponds to the greatest costs in investments and operation, being responsible for around 50–75% of the capital costs. Therefore, many large companies are seeking to optimize the synthesis gas generation stage, in order to make the GTL technology commercially viable.

In any manner, the reduction of costs of any stage is still the principal objective of all companies developing GTL. The use of catalytic membranes and compact reformers represent considerable advances in the area. Another possibility is in the elimination of the isomerization unit, which would occur if the Fischer–Tropsch catalysts were able to generate isomerized products. The addition of Brönsted acid sites to the traditional cobalt catalysts appears to be an interesting research option that is still under-explored.

However, it is fundamental to highlight that GTL processes are currently highly viable. If one compares the GTL route with those of a new refinery, it is clear that GTL is more attractive, even without the premium payment for better quality diesel. This situation can be seen in Table 1. The GTL route, creating higher quality products and in greater quantities, generates higher revenue than a refinery. If, to this fact, one adds the possibility that a premium of around US$ 3–4 per barrel of diesel would be paid for a product with insuperable qualities (cetane 75, zero sulfur and aromatics), the advantages of the GTL route become even more evident.

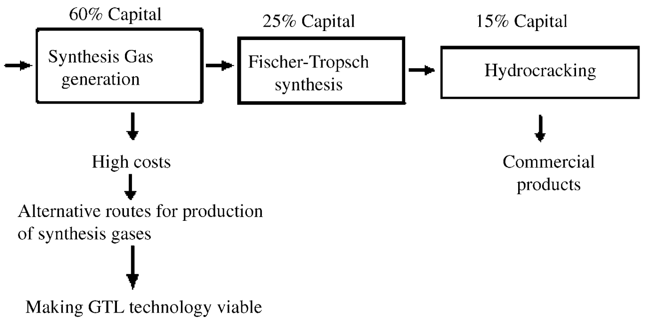

Fig. 6. Typical stages in GTL technology.

Table 1
Revenue relative to a GTL process and a new refinery

| | US$ (per barrel) | GTL | | Refining | |
|---|---|---|---|---|---|
| | | Profit (%) | Revenue (US$ per barrel) | Profit (%) | Revenue (US$ per barrel) |
| LPG | 16 | 5 | 0.8 | 4 | 0.64 |
| Naphtha | 19 | 25 | 4.75 | 3 | 0.57 |
| Gasoline | 20 | | | 12 | 2.4 |
| Medium distillate | 27 | 70 | 18.9 | 65 | 17.55 |
| Fuel oil | 18 | | | 7 | 1.26 |
| Coke | 0 | | | 9 | 0 |
| | | 100 | 24.45 | 100 | 22.42 |

## 5. Direct synthesis

The works of Wang et al. [16], which began in 1993, demonstrated the possibility of producing aromatics and hydrogen directly from natural gas, using for this molybdenum supported ZSM-5. From these pioneering studies, much attention has been given to this route, which avoids the high costs related to the transformation of natural gas into synthesis gas.

Claridge et al. [17] showed that Mo and W carbides are efficient catalysts for the conversion of methane into synthesis gas. In addition, various articles [18] proposed the use of highly dispersed Beta $Mo_2C$ supported ZSM-5 as a very active and selective catalyst for aromatizing methane. The search for additives, such as Ru, Pt, W, Zr, Co, Fe and Cr, to increase activity and stability has also been reported, turning this into an excellent area for research in the preparation of new catalytic systems. However, up to now, problems related to low conversion and intense deactivations of the new zeolites have not been overcome.

## 6. Conclusions

The traditional objectives of the refining industry – high conversion, diesel or gasoline selectivity – are being reconsidered, because of the more rigorous environmental legislation. As a result, the search for alternative oil sources, capable of generating cleaner fuels, is directing traditional refineries to the use of natural gas, in what is known as C1 chemistry. Although this field is not new, the natural gas transformation routes are mostly catalytic, requiring great effort from catalysis researchers for both making traditional routes viable with new raw materials and also developing new paths. The scenario that is developing is, without doubt, highly challenging, but equally encouraging for those that labor in the area.

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