

# The Role of Catalysis in Replacing Oil by Renewable Methanol Using Carbon dioxide Capture and Recycling (CCR)

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**Abstract** Fossil fuels (coal, oil, gas) are nature's major gift to humankind. Use of coal followed by petroleum oil and natural gas since the dawn of the industrial revolution in the eighteenth century brought us into a modern and increasingly technologically adept society. Limited resources, primarily depleting petroleum oil reserves and increasing world population and its demand for better standard of living, has already led to the end of cheap petroleum oil. Despite new oil discoveries, better technology, savings, efficient use etc., we must in the following decades wean ourselves out of our dependence on oil. Synthetic oil and hydrocarbons derived from coal and natural gas based on Fischer–Tropsch syngas chemistry have been at times used since the 1920s but the processes are costly, complex and limited. I have with my colleagues proposed and developed a new “Methanol Economy” approach based on metgas ( $\text{CO}-2\text{H}_2$ ) to methanol via bi-reforming or oxidative bi-reforming of shale or natural gas as well as carbon dioxide capture and recycling. Methanol can serve as a fuel and feed-stock to replace petroleum oil. Heterogeneous catalysis is playing key role in this fast developing field, which serves to achieve the quest for petroleum oil independence, one of the major challenges of our time. The scope and progress toward renewable methanol chemistry from the laboratory to practical industrial use are discussed.

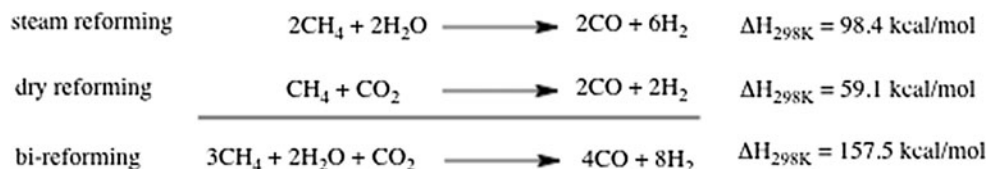
**Keywords** Renewable methanol · Metgas · Bi-reforming · Oxidative bi-reforming · Heterogeneous catalysis

Petroleum oil ever since realization of its significance in the latter part of nineteenth century became an essential energy and fuel source as well as raw material for varied chemicals and materials. Derived hydrocarbon chemistry developed into a significant and an extensive field [1]. Petroleum oil, while nature's most valuable gift, is however not going to last for long. It is argued whether we may have already reached the tipping point between oil production and consumption; although discovery of new reserves through new technologies producing shale and heavy oil give some relief, by the end of the twenty-first century, petroleum oil certainly will become scarce and therefore too expensive to maintain its dominant significance to our everyday life. We need therefore to find feasible, economically viable ways to replace petroleum oil. In our long-standing studies on petroleum chemistry in the last two decades, we increasingly focused our efforts on this essential but elusive challenge. Our efforts resulted in suggesting a feasible anthropogenic technological carbon cycle as well as developing much new chemistry relating to what is now called the “Methanol Economy”. A decade ago, I wrote a perspective in *Catalysis Letters* [2] and subsequently, two essays in *Angewandte Chemie* [3, 4] about the potential of a synthetic carbon cycle for replacing oil by methanol involving  $\text{CO}_2$  recycling chemistry (carbon capture recycling, CCR). Our research is reported in a monograph [5], and numerous publications [6–8], as well as patents [9–12]. It slowly became accepted that renewable methanol based chemistry (based on capture and recycling of carbon dioxide) is a feasible way to gradually replace diminishing

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petroleum oil resources. It offers a feasible solution to our oil conundrum and related environmental challenge of excessive CO<sub>2</sub> build-up in our atmosphere. Use of anthropogenic carbon recycling necessitates significant energy use, which can come from any source including alternate energy (primarily solar, but also wind, geothermal etc., even atomic albeit, made safer) or from still available fossil fuel burning power plants preferably in their off peak period use.

In this perspective, attention is called to the key role of



catalytic processes to the suggested and developing replacement of oil through renewable methanol produced using an anthropogenic carbon cycle and making it technologically and economically feasible.

The practical synthesis of methanol was developed based on syn-gas (a mixture of CO and H<sub>2</sub>) in the 1920s in Germany in the context of the so-called Fischer–Tropsch chemistry [1]. It was originally based on coal but subsequently shifted to more convenient natural gas. The conversion of natural gas using steam or dry (CO<sub>2</sub>) reforming as well as partial oxidation produces H<sub>2</sub>/CO mixtures with a ratio generally between 3 and 1. However, to produce methanol, a specific 2:1 H<sub>2</sub>:CO mixture is needed, which we named *metgas* [7]. It is presently produced using conventional steam and dry CO<sub>2</sub> reforming processes necessitating multi-steps and varied adjustment to obtain the needed 2:1 ratio. Furthermore, CO<sub>2</sub> is added in modern processes to the syngas mixture to facilitate the subsequent methanol synthesis step.

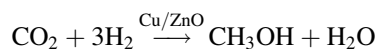
The used reforming processes are significantly endothermic. In modern processes (Topsoe, Lurgi, Linde and others), part of the natural gas is combusted in situ to provide the needed heat energy (autothermal reforming). It renders, however, the needed metgas production even more complex and costly (representing some 60 % of the overall cost of a methanol plant and production) including separation, purification and adjustments such as the water gas shift reaction.

In extensive studies, effective single step metgas formation was found to be challenging. To overcome these difficulties and complexity, we have however succeeded in developing a facile process called *bi-reforming* based on anthropogenic carbon dioxide recycling to produce metgas

from methane (natural gas) with CO<sub>2</sub> and steam in a single step by combining in essence the steam and dry reforming steps. Methane, CO<sub>2</sub>, and steam in a 3:1:2 ratio is reacted over a catalyst typically prepared from NiO deposited on MgO and activated with H<sub>2</sub> to provide the active supported Ni–Mo catalyst (or related supported metal/metal oxide catalysts). Bi-reforming is preferentially carried out under 5–40 atm pressure at 800–950 °C in a pressurized tubular flow reactor [7, 8].

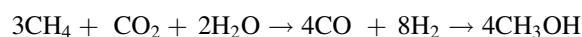
Practical simplified and economic methanol production can also be achieved by carbon dioxide capture and its chemical hydrogenative conversion or by selective oxygenation of methane or its source materials. Effective catalytic processes are essential in rendering these technologies economically feasible.

CO<sub>2</sub> capture from natural or industrial sources and its subsequent conversion to methanol involves either catalytic hydrogenation or bi-reforming. The needed hydrogen for catalytic hydrogenation is produced either from available hydrocarbon sources or by electrolysis or other cleavage of water with any available suitable energy. One-third of the used hydrogen produces water as a byproduct.



The catalytic hydrogenation of CO<sub>2</sub> was extensively studied and reported and need not be discussed here.

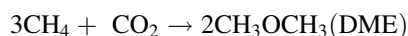
The methanol synthesis from CO–2H<sub>2</sub> (metgas) over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst is well recognized. Our new bi-reforming process [7–12] uses still available extensive natural gas (methane) sources with recycled CO<sub>2</sub> and steam in a single step catalytic process to produce metgas for subsequent by methanol synthesis.



Methanol can subsequently be dehydrated to dimethyl ether (DME) an efficient diesel fuel or household (heating) gas substitute.



If needed, water can also be recycled allowing the production of DME from methane (natural gas) while using only CO<sub>2</sub>.



Much effort over the years was put into the selective oxidation of methane (natural gas) to methanol. Numerous publications and patents claimed some success but only under extreme conditions (very high dilution with excess methane, short contact time, low temperature, low turn-over etc.) and generally only with very low conversions [1, 6]. Attempts to increase yields inevitably resulted in loss of selectivity. Therefore, effective oxidative synthesis of methanol by direct methane (natural gas) oxidation was considered not feasible because the thermodynamically favored formation of further oxidation products i.e. formaldehyde, formic acid and eventually carbon dioxide is inevitable.

Recently, there has been significant increase of natural gas (methane) sources with the discovery and use of shale gas reserves, as well as coal-bed methane, “tight” gas and potentially methane hydrates. These reserves are conservatively estimated to last well into the next century although their safe and economic recovery remains a challenge.

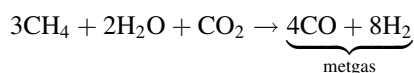
An essential challenge of hydrocarbon chemistry is to convert methane to methanol by the overall insertion of a single oxygen atom (oxygenation) in high yield and selectivity with no other oxidation by-products formed.

We recently succeeded and reported a breakthrough for the exclusive self-sufficient conversion of methane (natural or shale gas as well as other source materials) to metgas for subsequent methanol synthesis. We have termed the overall exclusive *oxygenation* of methane to methanol as *oxidative bi-reforming* [8, 12]. Oxygenation (i.e. oxygen functionalization) is insertion or substitution of oxygen into a hydrocarbon that is essentially different from conventional oxidations [1].

Reforming processes including bi-reforming are highly endothermic generally necessitating substantial external energy. In modern methanol plants, auto-thermal reforming is overcoming this difficulty using partial in situ oxidation of part of the feed natural gas. In our oxidative bi-reforming process separate complete combustion of an equivalent of methane (natural or shale gas, other methane sources) with  $\text{O}_2$  from the air gives the needed reaction heat. At the same time, it also provides the required  $\text{CO}_2$ – $2\text{H}_2\text{O}$  (steam) mixture, which is captured and mixed with 3 equivalent of fresh methane (natural gas) giving the needed specific feed for bi-reforming to provide exclusively metgas for the subsequent methanol synthesis step.



admixing fresh methane followed by bi-reforming

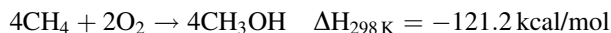


$$\Delta H_{298\text{K}} = +157.5 \text{ kcal/mol}$$

methanol synthesis



overall reaction



Auto-thermal reforming of methane with in situ partial oxidation of the feed natural gas involves costly multi-steps of separation and adjustment for obtaining the 2:1  $2\text{H}_2$ – $\text{CO}$  syn-gas mixture. This represents 60 % of the cost of a modern methanol plant. Oxidative bi-reforming of methane (and its source materials), in contrast, substantially decreases the complexity and thus the cost to prepare metgas for subsequent methanol synthesis. It also provides the needed reaction and process heat and significantly recycles  $\text{CO}_2$  into methanol production eliminating atmospheric pollution.

Overall, the oxidative bi-reforming of methane followed by the methanol synthesis step effectively achieves in a simple, self-sufficient way the exclusive oxygenation of methane to methanol in high yield and selectivity without any oxidation byproducts or losses—a longstanding and major challenge in hydrocarbon chemistry [1].



Oxidative bi-reforming of methane to metgas can be carried out in separate or in a single multi tubular reactor allowing separate combustion of an equivalent of methane with the oxygen of air [8, 12]. The generated heat and the exhaust  $\text{CO}_2$ – $2\text{H}_2\text{O}$  gas mixture is captured and admixed with 3 equivalents of fresh methane. The preferred catalyst for bi-reforming typically is Ni/MgO prepared from 15 % NiO deposited on/MgO and activated with hydrogen at 800–900 °C. Other possible catalysts include metal or metal oxide such as V, Ti, Ga, Mg, Cu, Mo, Bi, Fe, Mn, Co, Nb, Zr, La or Sn, and their corresponding oxides. Bi-reforming is carried out under 5–15 atm pressure and 800–950 °C temperature. Metgas formed in high yield and selectively is subsequently converted in the well-known and industrially widely practiced methanol synthesis over a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> or related catalysts, thus giving pure methanol.

The overall *oxidative bi-reforming* of methane (or its source materials) represent a new feasible way for its effective and selective oxygenation to methanol [8–12]. Methanol produced from still abundant natural or shale gas resources can be used as a replacement for petroleum oil and its derived products in an economic way within the framework of our previously developed “Methanol Economy” concept [5]. Eventually when methane and other fossil fuel sources will be exhausted carbon captured and recycled from the atmosphere and hydrogen generated from water will be able to provide methanol.



The “George Olah Carbon dioxide to Renewable Methanol Plant” of Carbon Recycling International in Iceland based on local geothermal energy. The first commercial carbon dioxide recycling plant operating in the world. “Reprinted with kind permission of K. C. Tran, CEO, Carbon Recycling International, Iceland”

Methanol and DME, beside being excellent transportation fuels, also allow storage and transportation of hydrogen and thus energy. They are also raw materials for subsequent conversion to varied essential chemicals, such as ethylene, propylene and their derived products. They allow producing essentially all products presently made by the petrochemical industry from oil or natural gas.

The concept and developed related new chemistry and technology of renewable methanol production are increasingly gaining industrial acceptance in different parts of the world such as China, the Mid-East, and to some extent Europe (see Picture of the first operating CO<sub>2</sub> to methanol recycling plant in Iceland). Interest is also starting to increase in the US and other countries. Catalytic chemistry is playing a key role in this fast developing field, which aims at oil independence—one of the major challenges of our time.

The foundations of an effective and practical carbon dioxide capture and recycling (CCR), which convert CO<sub>2</sub> into renewable methanol, have been laid and are being increasingly translated into practical industrial use. For the rest of the century, the use of natural (shale) gas and other methane sources will continue. When such sources are depleted, capture of CO<sub>2</sub> from our atmosphere and water cleavage providing the required hydrogen for recycling CO<sub>2</sub> will be powered by renewable (mostly solar) or

atomic energy sources. We can replace petroleum oil and eventually all fossil fuels by renewable methanol chemistry through CCR. At the same time, we will be minimizing the harmful environmental effects of excessive CO<sub>2</sub> emissions effecting the global climate change. Technological carbon-capture and recycling (CCR) offers a sustainable and practical solution to our carbon conundrum.

Professor G. K. Surya Prakash, my former student, my friend, and for the past 30 years, my colleague and partner played an essential role in our work on the methanol economy and renewable methanol chemistry. His contributions and increasing leadership of our joint research team were essential. I also thank our colleagues, who participated in our efforts, primarily Dr. Alain Goepfert, as well as Drs. Thomas Mathew, Miklos Czaun, Robert Aniszfeld, Sergio Meth, Patrice Batamack and other members of the Loker Hydrocarbon Research Institute. Their names are found in the references of our papers, patents, and monographs. The USC Loker Institute supported much of our research together with more recent support from the Hydrocarbon Research Foundation and the U.S. Department of Energy, which is gratefully acknowledged. Intellectual property rights related to the Methanol Economy and its applications are protected and belong to the University of Southern California.

## References

Selected recent references are given. Also references to further reading of our work to replace oil with renewable methanol using new catalytic chemistry are included. They also credit the fundamental Fischer–Tropsch syngas chemistry, which for nearly a century was the basis of synthetic hydrocarbon chemistry.

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