Obituary Note
The Latest Environmental Contributions of John O’Mara Bockris

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Abstract
While widely acknowledged as the father of the Hydrogen Economy and worthy to be dubbed as grandfather of the Methanol Economy, John O’Mara Bockris (JOMB) continued to inspire important environmental advances to the end of his most creative life. His co-invention of what may turn out to be a ground-breaking US Patent 8,413,420 helps to open the way to capturing CO₂ from automotive exhausts and its conversion to recyclable methanol fuel, thereby greatly reducing and possibly even reversing global warming. Most recently, in a letter dated shortly before his death, published herein as the Appendix, JOMB pointed to inexpensive mass production of methanol from natural gas via the syngas route which may lead to the displacement of gasoline by methanol as the main automotive fuel and to major reductions in global CO₂ emissions.

Keywords: Catalysts for methanol synthesis, Converting captured CO₂ to methanol, Methanol from natural gas, Methanol synthesis reactor, Syngas by steam reforming

1. Introduction
Although Prof. John O’Mara Bockris, hereafter referred to as JOMB, has been widely recognized as the father of the Hydrogen Economy [1–3], he might also be dubbed as the grandfather of the Methanol Economy, having anticipated Nobelist George Olah [4] by some thirty years [5,6]. Their outstanding achievements in these fields through the first decade of this century are best summarized by JOMB [7] and Olah et al. [8].

JOMB’s latest environmental contributions included co-invention with S. Zaromb of the recently issued US Patent 8,413,420 [9], which opens the way to the capture of CO₂ from motor vehicle exhausts and its conversion to methanol, possibly in repetitive cycles, thereby minimizing their atmospheric CO₂ imprint and thus slowing down or possibly even reversing global warming. As a follow-up to that invention, we reproduce in Appendix his letter of June 13, 2013, written shortly before his death, which inspired a further potential advance that is the focus of this paper.

In the italicized portions of the Appendix, JOMB pointed out that:

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The recent and expected continued fall in natural gas prices opens the possibility of highly reduced costs of methanol production from steam-reformed natural gas via the reactions

\[ \text{CH}_4 + 2\text{H}_2\text{O} \rightarrow 4\text{H}_2 + \text{CO}_2 \]  

(Appendix, JOMB’s “appropriate equation”), \hspace{7cm} (1)

\[ 3\text{H}_2 + \text{CO}_2 \xrightarrow{\text{CuZn}} \text{CH}_3\text{OH} + \text{H}_2\text{O} \text{ (CH}_3\text{OH from CO}_2, \quad \Delta H \approx 130 \text{ kJ/mol CH}_3\text{OH}). \]  

(2)

As compared with the cost of 20–30 $/GJ for the currently used electrolytic generation of the \( \text{H}_2 \) that is required by reaction (2), the costs entailed by reaction (1) should be less than 6 $/GJ.

Although reactions (1) and (2) would not result in any net removal of \( \text{CO}_2 \), their implementation will yield a methanol fuel that will be more competitive than gasoline at current prices by a wide margin.

Indeed, JOMB’s estimate of <6 $/GJ for methanol from steam reformed gas translate to less than 0.9 $/gallon, as compared with current methanol and gasoline prices of about 3 $/gallon and 3.4 $/gallon, respectively. JOMB’s “appropriate equation” results from steam reforming natural gas

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \text{ (syngas by steam reforming, input } \approx 250 \text{ kJ/mol CH}_4) \]  

followed by the water gas shift reaction [10,11]

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2. \]  

Moreover, even more promising results are obtained with inclusion of the following key reaction:

\[ \text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH} \text{ (methanol from syngas, } \Delta H \approx 128 \text{ kJ/mol CH}_3\text{OH}). \]  

Reactions (2), (3), and (5) can be combined in the ratio of 1:3:3 so as to yield substantially pure methanol

\[ 3\text{CH}_4 + 2\text{H}_2\text{O} + \text{CO}_2 \rightarrow 4\text{CH}_3\text{OH}, \]  

which implies no need of substantial electric power input to generate methanol from natural gas and captured \( \text{CO}_2 \) (vide infra). It also implies that captured \( \text{CO}_2 \) can also be converted to methanol in the same process without need of much additional electric power input.

The following section outlines some steps and modifications required for successful implementation of reactions (2), (3), and (5).

2. Methanol from Natural Gas and Carbon Dioxide

Of reactions (2), (3), and (5), only the steam reforming reaction (3) is endothermic, requiring a heat input of about 250 kJ/mol of \( \text{CH}_4 \). That heat might be supplied by the exothermic reactions 2 [\( \Delta H \approx 130 \text{ kJ/mol CH}_3\text{OH} \)] and 5 [\( \Delta H \approx 128 \text{ kJ/mol CH}_3\text{OH} \)] by having all three reactions set to run together in an optimal ratio in a methanol synthesis reactor. This would result in up to a mole of captured \( \text{CO}_2 \) being used up per 4 mole of generated \( \text{CH}_3\text{OH} \).

Much of the vast amount of research on optimizing the catalysts and temperature cycling for the most practical utilization of the preceding reactions has been reviewed by Song and Pan [12] and more recently in a paper by Olah et al. [9], both of which teams caution about the care needed to avoid rapid deterioration of catalysts and point to the possibility of reactions (2), (3), and (5) being set to occur together. Moreover, Olah et al. [9] have arrived at reactant ratios similar to those of reaction (3) and (5) albeit by altogether different routes.
3. Conclusions

With the availability of large supplies of natural gas at reduced prices, the possibility arises of mass producing low cost methanol via the syngas route thereby displacing gasoline as the main automotive fuel and also reducing global warming by cleaner burning and by reduced costs of converting captured CO\textsubscript{2} to methanol.

This latest development inspired by JOMB’s letter dated less than a month before his death may turn out, if put into practice, to be a crowning environmental contribution of his illustrious career.

Appendix . JOMB’S Letter Dated June 18, 2013 [Unedited but with Parts in Italics]

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June 18, 2013

Dear Sol:

I have recently written to you about our possible patent not yet in our name and I have written as a helpful note to ask Mr. Langel to tell us what we might do to increase the legal status of my name in the patent. I know that the certificate of correction has been written although there is still the idea that I am supposed to write an added note to the certificate of correction which I have not done. (Should I do it, where should I send it, etc.?)

However, this note today is rather different, though not entirely unrelated, - suggestion which could be much worth a patent than what we have tried so far.

I’m referring to the fact that natural gas prices have dropped by 25 percent in recent times and the findings are such that it’s supposed to stay like that for at least twenty or thirty years. The supplies are enormous now and we should be exporting natural gas for many years.

Now, see what this means. If we steam reform natural gas, – a common reaction, the appropriate equation is:

\[
\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow 4\text{H}_2 + \text{CO}_2
\]

Now, the formative equation for the desired methanol is:

\[
3\text{H}_2 + \text{CO}_2 \xrightarrow{\text{CuZn}} \text{CH}_3\text{OH} + \text{H}_2\text{O}
\]
You will see then that what we produce from the natural gas steam reformed is pretty much what we need for synthesizing methanol. Yes, there would have to be a pressure change and a small amount of heat up to 300°C whereupon the reaction occurs, perhaps another 50°C might be helpful.

Now the point of the note to you is the cost of course. Made in the normal way whereby one could obtain the hydrogen from water by electrolysis of course goes up tremendously and three estimates I have made have costs between $20 and $30/ GJ.

In respect to this suggestion, - that the desirable methanol should be made from natural gas, I have not had a professional estimate of its cost but as it comes from $3/GJ natural gas, it can hardly be more than, say, $6/GJ. This would look after the heating and the high pressure. Thus, when comparing $6/GJ for our new methanol with $25 for the one which got the hydrogen from water. Of course there is a penalty to be paid for this enormous attractive decrease in price and that is if we do it from CH4, we’re not going to remove a molecule of CO2 from the atmosphere when we make methanol and therefore it is not a global warming property.

On the other hand, as Olah has been stressing for many years, methanol in itself alone is a very worthy fuel and it was indeed suggested by me for the first time in 1975.

So now we’re going back to creating methanol, – just methanol, – but its cost is only $6/GJ.

Now can you convert $/GJ to $/Gallon. I think that if we go down by four times from $25 to $6, and as the methanol earlier was to cost $4/GJ, the new methanol from natural gas would cost less than $/Gallon!

Now, if I am right here, we certainly ought to make a patent because of course methanol is an extremely worthy fuel. Indeed Olah has been on this without any global warming properties for some years apart from my 1975 suggestion.

Please give this your own thought and whether my reasoning is reasonable and then we can consider what should be done about it!

I have always said that the only way to beat ExxonMobil will be to produce something cheaper than gasoline and that is what we have done here!

My best wishes.

Sincerely,
John O’M. Bockris
Distinguished Professor, Department of Chemistry
Texas A&M University, 1978–1997
Professor, Department of Chemistry, University of Pennsylvania, 1953–1972

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References


