

Development Potential of a New Natural Gas-to-Liquid Conversion Process

Michael Golombok*

Shell International Exploration and Production, Volmerlaan 8, 2288 GD Rijswijk, The Netherlands

Tom Nijbacker and Maria Raimondi

Avantium Technologies, Zekeringstraat 29, 1012 TX Amsterdam, The Netherlands

We determine the carbon selectivity for single-step conversion of natural gas to an acetic acid/methanol liquid mixture by a new homogeneous catalytic process. The amount of CO₂ produced as a byproduct needs to be less than 25% of the total product for the process to be of interest for industrial development. Using a combination of nitrogen blank runs and ¹³C labeling along with gas chromatography and mass spectrometry, we show that (1) a lower pressure of methane gives better conversion, (2) most of the CO₂ produced comes from decomposition of the trifluoroacetic acid solvent, (3) the reaction is quicker than previously thought, and (4) the product selectivity to liquids is typically around 75%.

1. Introduction

Many oil wells emit considerable quantities of hydrocarbons in the form of associated natural gas.¹ This gas is either vented or flared. Because methane is a considerably worse greenhouse gas than carbon dioxide, flaring is probably the lesser of two evils.² Nonetheless, the desirability of emissions reduction and the waste of a resource make it desirable to recover this natural gas in some form. In addition to gas associated with oil wells, there are also billions of barrels of oil equivalent of energy locked in gas fields contaminated with CO₂.³ In both stranded and associated gas cases, the resource is often remote from market, so it cannot simply be piped to a customer; the scale, distances, and local infrastructure mean that collection for pipeline distribution is not a viable option. Normal physical gas-to-liquid processes involve compression to liquefied natural gas and are only worth doing on a large scale for dedicated gas wells as opposed to gas associated with oil production.⁴ Similar considerations apply to the only chemical gas-to-liquid conversion currently applied for natural gas conversion from a well outlet: a two-step distillate synthesis.⁵ In the past few years, a number of reports^{6–11} have appeared aimed at converting methane to acetic acid by coupling it to CO₂. In these studies, it is necessary to distinguish between three types of possible reaction mechanisms:

A. Methane and CO₂ are added as reactants and couple together to form acetic acid.

B. Methane couples to CO₂, which derives from the carboxylate decomposition of the trifluoroacetic acid (TFA) solvent.

C. The carboxylate group on the acetic acid originates from methane and subsequently couples to another methane-derived moiety. The oxidation of methane is enabled by the K₂S₂O₈ oxidizer, which has been shown to be a vital component of this reaction; without it, there is no acetic acid produced.^{6,11}

The coupling of methane and CO₂ to form acetic acid is extremely unfavorable from a thermodynamic viewpoint.¹⁰ A simple thermodynamic calculation shows the equilibrium to be such that the fractional conversion is on the order of 10⁻⁸. Work by Hoechst claimed¹² to enable reaction A, and at the low concentrations determined by thermodynamics, conversion has been observed.^{13,14} Nonetheless, studies seem to indicate that significant acetic acid can be generated from methane; however, careful labeling studies are required to identify each of the mechanisms A–C above, and these indicate finally that mechanisms B and C predominate. To this end, it is important to understand whether the process will help sequester CO₂ in order to be of interest.

From an industrial viewpoint, reaction A would be highly desirable as a way of sequestering CO₂ from contaminated gas reservoirs during production while simultaneously enabling a gas-to-liquid single-step chemical conversion, which would be ideal for the stranded gas fields that contain large amounts of CO₂. Reaction B, on the other hand, is clearly of no interest because, on a large scale, the use of TFA would not be practicable and a substitute would have to be found. One is therefore left with mechanism C, a process that does, nevertheless, still turn methane into a high-density transportable liquid and so remains of interest. The process is thus still of interest for dealing with natural gas, for example, at the associated production sites described above.

In all previous reports of this effect, all attention has been focused on the liquid solvent phase, which is where the conversion reaction takes place. No attention has been paid to any byproducts in the gas phase above the solvent. In this paper we examine these gaseous byproducts. This is important because if a lot of CO₂ byproduct is found in the gas phase, then the conversion of methane to a liquid is not acceptable from environmental and sustainability viewpoints. The crucial comparison has to be whether there is a significant reduction in CO₂ compared to simply flaring the natural gas; i.e., how much net CO₂ is produced in the process? Previous studies have not examined this issue.

* To whom correspondence should be addressed. Tel.: 31 70 447 2327. Fax: 31 70 447 3366. E-mail: michael.golombok@shell.com.

B

There are general standards on this so-called carbon selectivity to liquid product and CO₂.¹⁵ These depend on the conversion of methane X and the product selectivity for component i S_i defined by

$$X = \frac{n_{\text{CH}_4} - n_{\text{CH}_4}}{n_{\text{CH}_4}}; \quad S_i = \frac{n_i}{\sum n_i}$$

where n_i is the number of moles of product component i and n_{CH_4} is the number of moles of methane at the start of the experiment. Generally, a natural gas conversion defined by $X > 30\%$ is considered to be required for industrial practicality with an associated liquid product selectivity $S = 70\text{--}85\%$, with the range in the selectivity being a measure of the stringency criteria across different types of industrial practice.^{16,17} Correspondingly, the maximum acceptable selectivity for CO₂ is around 25%.

Previous studies of the single-step methane to acetic acid/methanol mixture do not address the issue of how much of the products of methane conversions are gaseous. In this work, we determine the carbon selectivity of the reaction. Section 2 discusses the experimental method, and section 3 reviews the results.

2. Experimental Section

2.1. Reaction Equipment. A reactor assembly consisting of four parallel Hastalloy C276 autoclaves with independent precision control and monitoring devices was used. Each reactor was equipped with overhead stirring, a thermocouple for temperature measurement, an internal heater coil for precision temperature control, a pressure transducer, and a mass flow controller. A Julabo thermostat additionally provided the reactors with a common heating mantle, set at a temperature slightly lower than the required reaction temperature. In combination with the internal reactor heating coils, this produces an effective “push–pull” temperature control system. Reaction exotherms can be counteracted, keeping the reactor temperatures constant. The power supplied to the heating coils reflects the processes occurring and can also be logged against the reaction time.

The reactants were obtained from Sigma Aldrich. The TFA purity was 99%. The ¹³C-labeled methane was obtained from Spectra Gases and had 99.9% purity. The mass flow controllers were calibrated in order to measure the precise amount of CH₄ (both for labeled and unlabeled reactants) added to the reactors. The total gas volume of the reactor was measured to be 74.5 mL at ambient conditions.

As in previously reported experiments,^{6,9} to convert methane to acetic acid in a single-step reaction, a catalyst [0.13 mmol of vanadium(V) oxide] and promoter oxidizer (25 mmol of K₂S₂O₈) were dissolved in 40 mL of TFA. The V₂O₅ catalyst was suspended in a portion of TFA and treated with ultrasound for 15 min prior to addition to the reactor, to help with breaking up of the larger catalyst particles. The reactor was then closed tightly, using Teflon O rings, to avoid any leaks. The reactor was purged three times with 30 bar of nitrogen and fast (800 rpm) stirring. During purging, the gas was sampled on an Agilent 5973N real-time gas analyzer and the oxygen content was observed to decrease to less than 1000 ppm.

The temperature and pressure of the reactor, as well as the mass flow controller readings during methane addition, were monitored throughout. The reactor was filled to 1 bar with nitrogen followed by either 5 or 20 bar of methane at room temperature with stirring at 800 rpm. Then the reactor contents were heated to 80 °C with continuous stirring. At the end of the reaction time, which unless otherwise stated was 16 h, the reactor was cooled to room temperature.

2.2. Product Analysis. ¹H NMR analyses were performed on the liquid mixture after completion of the reaction. The liquid products from the reactions were analyzed by ¹H NMR (400-MHz machine). Samples were accompanied by calibration samples containing known quantities of acetic acid and methanol, so that the products could be quantified accurately. The principal products were acetic acid and methanol (or the methyl ester of TFA). Typically, acetic acid gave an NMR signal at a frequency shift of 2 ppm, and methanol gave a signal at a frequency shift of 4.1 ppm.

The full depressurized reactor gas volume (34.5 mL) was emptied into a 12-L Tedlar bag, allowing time for full desolubilization of the gases with fast stirring. The volume of gas in the Tedlar bag was measured by water volume displacement when the bag was inserted into a 2-L measuring cylinder, and 1 L of water was added. The total number of gas moles after reaction could then be calculated from the ideal gas law.

From gas chromatography (GC) analysis, the molar/volume percent composition of the product gas was obtained by injecting a portion of the Tedlar bag volume into a GC analyzer, an Interscience Trace GC 2000 instrument, with a thermal conductivity detector. A known gas mixture was used to calibrate peak areas and enable accurate CH₄ and CO₂ quantification. Mass spectrometry (MS) was conducted on a V&F Airsense 2000 instrument, using low, medium, and high ionization energies to ensure the detection of all gas-phase products (CO₂ was only detected using the high ionization energy setting). ¹H and ¹³C NMR analyses were conducted using a Bruker Avance 400 NMR spectrometer.

The final number of moles of methane in the reactor could then be calculated, and the difference with the initial number of methane moles (calibrated mass flow controller measurement) yielded a value for the total methane conversion. The difference between the total methane conversion and the yield of liquid products (from NMR) corresponds to the yield of CO₂, with the GC analysis not showing any significant quantities of other gases.

3. Results and Discussion

Figure 1 shows the yield of liquid products and CO₂. The yields of liquid product decrease with pressure, and the selectivity to acetic acid appears to decrease with pressure. These yields are all significantly above those based on equilibrium coupling as discussed for mechanism A above. This is in itself proof that the other mechanisms B and C are the important ones here. Although occasional very small amounts of CO were seen, this was on the limits of detectability, and the only gaseous product was CO₂. The gas mass balance is discussed below (Figure 3), and as in previously reported experiments, the only liquid products observed were methanol and acetic acid, plus some associated ester and anhydride formed from solvent interaction for which we

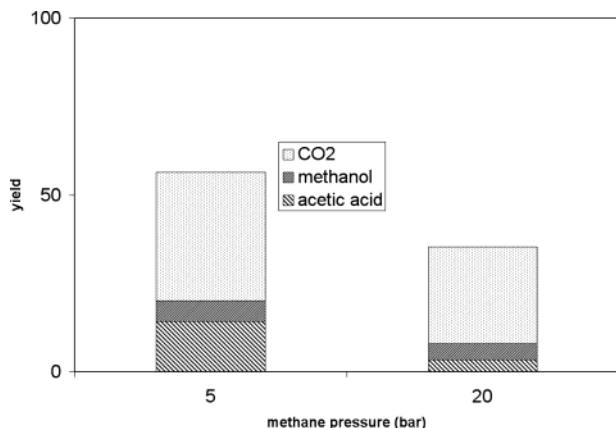


Figure 1. Methane conversion and yield of gaseous and liquid products at two different pressures.

corrected. The increasing quantities of methane measured with pressure confirmed our liquid observations of decreasing conversions with increasing pressure. (As a result, further experimental studies were confined to 5 bar.) The CO_2 selectivities are 65% of the product at 5 bar of methane pressure and 78% at 20 bar of methane pressure. This would seem to indicate that the process totally fails on the criterion mentioned in the Introduction, i.e., that the CO_2 should be less than 30% of the product. However, a number of observations have caused us to question whether all of the CO_2 really results from methane reaction. In particular, recent work by Wilcox et al.¹⁰ and our own measurements here indicate that substantial amounts of the observed CO_2 actually originate in the decomposition of TFA. To show this, we ran “blank” experiments using pressurized nitrogen instead of methane and keeping all of the other conditions the same as those in the other experiments. This showed that, over the reaction time of 16 h at 80 °C, up to 1% of the TFA solvent decarboxylates, producing enough CO_2 gas to account for a large portion of the CO_2 formed in reactions using methane. (This also allows for the fact that we have previously shown that a large fraction of the CO_2 is dissolved in the solvent.¹⁸)

The source of TFA decarboxylation reactions probably arises from the presence of electron-withdrawing groups such as $-\text{CF}_3$. The TFA decarboxylation sheds new light on the reaction mechanism because it would appear that TFA is a probable source for both CO_2 gas and the carboxyl group for acetic acid. If this is the case, acetic acid could, at least in part, be composed of one carbon originating from methane and one carbon originating from the TFA solvent.

We have thus established that a considerable portion of the CO_2 does not originate from methane. We now use ^{13}C labeling of the methane to evaluate how much does actually originate just from methane. Nonetheless, because the reaction medium is producing CO_2 , it would mitigate heavily against further development were it not for the fact that we have also found that we can run this reaction on a time scale considerably shorter than the 16 h that we and a number of other workers have typically used.⁶ The evidence from this comes from monitoring the pressure during the reaction; this is shown in Figure 2 for a typical run at 5 bar of methane pressure. The local minimum at around 3 h of run time, corresponding to around 50 min after the reaction temperature was reached, indicates that methane gas has been consumed but not enough CO_2 has been produced to compensate for it. The latter does, however,

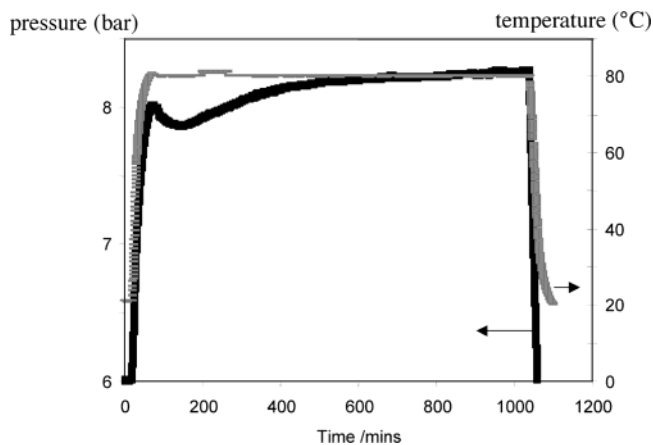


Figure 2. *PT* profile during an experiment with 5 bar of methane.

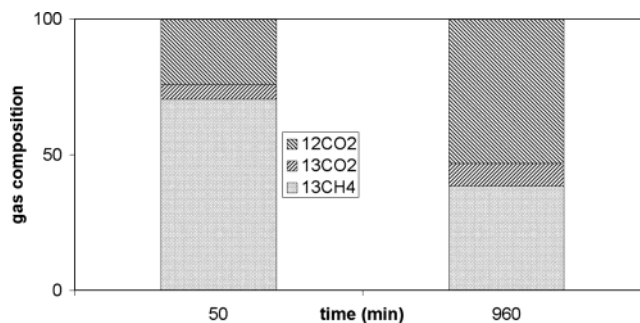


Figure 3. Gas cap contents for short- and long-duration experiments showing a volume composition of product gases.

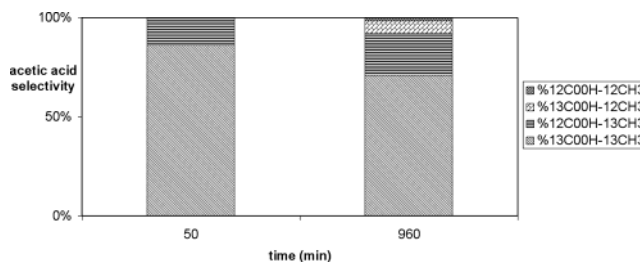


Figure 4. Relative amounts of labeled acetic acid products determined from ^{13}C NMR.

appear to take place during the remainder of the 16 h of the experimental run. Figure 2 thus suggests that there are two sequential processes taking place: first a fast oxidative coupling followed by a more prolonged slower oxidative process.

These two observations—the formation of CO_2 from TFA and the fairly rapid consumption of methane before TFA decomposition comes into play—formed the basis for our subsequent experiments. These consisted of the application of isotope labeling ($^{13}\text{CH}_4$) to determine the gas and liquid phase products truly arising from methane. Figure 3 shows the gas-phase product distribution. Although the relative amount of labeled CO_2 (arising from the labeled methane) does not change very much during the long experiment, compared to the short one, methane is consumed and a lot of unlabeled CO_2 is produced. The auto-oxidative experiment is thus essentially complete in the 50-min run time of the short experiment.

To assess the true products of the reaction, one needs to look carefully at the isotopic isomers of acetic acid; these are shown in Figure 4. The ^{13}C NMR analysis indicated that the majority of the acetic acid contained two ^{13}C atoms. For the shorter reaction time (50 min at

D

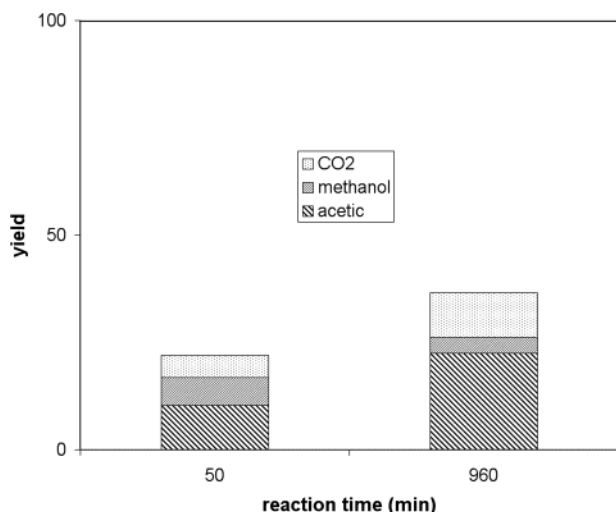
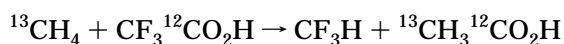


Figure 5. Total yields of acetic acid, methanol, and CO₂ at two different duration experiments.

80 °C), only 14% of the acetic acid incorporated ¹²C from the TFA solvent and no products contained ⁻¹²CH₃ groups. This would occur by the mechanism previously identified by Wilcox et al.¹⁰ and globally represented by



¹²CH₃ was, however, detected in small quantities (less than 10% of the acetic acid) after the longer reaction time of 960 min at 80 °C, and it is unclear how this was formed. A strict auto-oxidative coupling should, of course, have both carbons on acetic acid labeled; again we see that, between the short and long reaction times, most of the activity is associated with reaction with the solvent. At long reaction times, we start to see even species where the ¹²C methyl group has formed, a route that is difficult to envisage and which would require a whole sequence of exchange reactions. This regime is clearly not of interest for a natural gas-to-liquid process and is simply noted in passing as being purely of academic interest.

Combining the measurements, we may now obtain the overall product spectrum (Figure 5) yield for the auto-oxidative coupling of methane. The experiments showed that the relative amounts of acetic acid and methanol produced in the reaction depended on the reaction time. The longer reaction time favored the formation of acetic acid, while methanol was present in larger quantities after the shorter reaction time. This implies that methanol is an intermediate along the mechanistic pathway to the formation of acetic acid and is additional proof of the predominance of our auto-oxidative pathway (mechanism C above), where the persulfate oxidizes methane. Because the acetic acid selectivity actually turns out to increase with longer reaction times, this suggests that, at later stages of the reaction, the decomposed TFA starts to play an increasingly important role in the reaction, which may explain the confusing claims of coupling between methane and carbon dioxide. Thus, although more acetic acid is produced at the longer time, it is, as we saw above, substantially produced from interaction with the solvent. The CO₂ actually arising from methane only increases from 24% to 28%; however, viewed in terms of net CO₂ production irrespective of the source, the shorter time reaction just fulfils the required selectivity

criteria. The reaction at shorter time is of more interest from the point of view of running a continuous process anyway.

4. Conclusion

1. The reaction previously described as methane–CO₂ coupling is, in fact, an auto-oxidative coupling reaction, which can run only on methane.

2. The highest liquid yields with more selectivity to acetic acid occur at lower pressures although relatively more CO₂ is produced.

3. A significant portion of the CO₂ produced actually arises from the decomposition of the TFA solvent.

4. The reaction arising from methane and its oxidative products is substantially over in less than 1 h; subsequent production of acetic acid arises from interaction with the decomposition products of the TFA. The conversions are on the order of 25%, and the CO₂ selectivity is also around 25%, with the remaining 75% selectivity to liquid products. This reaction is thus on the border of the acceptability criterion for a practicable process.

5. If the process described here is to be further developed for industrial application on contaminated gas fields, then an alternative solvent would need to be found. TFA is expensive and difficult to handle and, as we have shown, interferes with the desired reaction. Similar considerations apply to the oxidant K₂S₂O₈. For example, an aerobic alternative would need to be developed.

Literature Cited

- Jaffe, D. A.; Honrath, R. E.; Furness, D.; Conway, T. J.; Dlugokencky, E.; Steele, L. P. A determination of the CH₄, NO_x and CO₂ emissions from the Prudhoe Bay, Alaska oil development. *J. Atmos. Chem.* **1995**, *20* (3), 213.
- Hemond, H. F.; Fechner-Levy, E. J. *Chemical fate and transport in the environment*; Academic Press: Boston, 2000.
- Golombok, M.; Chewter, L. Centrifugal separation for cleaning well gas streams. *Ind. Eng. Chem. Res.* **2004**, *43* (7), 1734.
- Senden, M. M. G.; Punt, A. D.; Hoek, A. Gas to liquids processes: current status and future prospects. *Stud. Surf. Sci. Catal.* **1998**, *119*, 961.
- Geerlings, J. J. C.; Wilson, J. H.; Kramer, G. J.; Kuipers, H. P. C. E.; Hoek, A.; Huisman, H. M. Fischer–Tropsch technology—from active site to commercial process. *Appl. Catal. A* **1999**, *186* (1 and 2), 27.
- Taniguchi, Y.; Hayashida, T.; Kitamura, T.; Fujiwara, Y. Vanadium catalyzed acetic acid synthesis from methane and carbon dioxide. In *Studies in surface science and catalysis*; Inui, T.; Anpo, M.; Izui, K.; Yanagida, S.; Yamaguchi, T., Eds.; Elsevier: Amsterdam, The Netherlands, 1998; Vol. 114, p 439.
- Nizova, G. V.; Suess-Fink, G.; Stanislas, S.; Shul'pin, G. B. Carboxylation of methane with CO or CO₂ in aqueous solution catalysed by vanadium complexes. *Chem. Commun.* **1998**, 892.
- Reis, P. M.; Silva, J. A. L.; Palavra, A. F.; Frausto da Silva, J. J. R.; Kitamura, R.; Fujiwara, Y.; Pombeiro, A. J. L. Single-pot conversion of methane into acetic acid in the absence of CO and with vanadium catalysts such as amavadine. *Angew. Chem., Int. Ed.* **2003**, *42* (7), 821.
- Zerella, M.; Muhopadhyay, S.; Bell, A. T. Synthesis of mixed acid anhydrides from methane and carbon dioxide in acid solvents. *Org. Chem. Lett.* **2003**, *5* (18), 3193.
- Wilcox, E. M.; Roberts G. W.; Spivey, J. J. Thermodynamics of light alkane oxidation. *Appl. Catal. A* **2002**, *226*, 317.
- Golombok, M.; Teunissen, W. A chemical alternative to natural gas flaring. *Ind. Eng. Chem. Res.* **2003**, *42*, 5003.
- Hoechst Aktiengesellschaft. Method of manufacturing acetic acid. World Patent WO 96/05163, 1996.
- Spivey, J.; Gogate, M. R. Method and catalysts for the manufacture of alkyl carboxylic acids by the carboxylation of lower alkanes. World Patent WO 99/59952, 1999.

(14) Wilcox, E. M.; Gogate M. R.; Spivey, J. J.; Roberts, G. W. Direct synthesis of acetic acid from methane and carbon dioxide. *Stud. Surf. Sci. Catal.* **2001**, *136*, 259.

(15) Periana, R. A.; Taube, D. J.; Evitt, E. R.; Loffler, D. G.; Wentrcek, P. R.; Voss, G.; Masuda, T. A mercury-catalyzed high-yield system for the oxidation of methane to methanol. *Science* **1993**, *259*, 340.

(16) Parkyns, N. D. Methane conversion—a challenge to the industrial chemist. *Chem. Br.* **1990**, 841.

(17) Hutchings, G. J.; Joyner R. W. Prospects for the partial oxidation of natural gas. *Chem. Ind.* **1991**, 575.

(18) Golombok, M. Differential solubilities of CO₂ and methane and the potential for coupling in TFA. *Appl. Catal A* **2003**, *253*, 537.

Received for review January 6, 2004
Revised manuscript received July 1, 2004
Accepted July 1, 2004

IE040012J