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J. W. CORNFORTH

1st November, 1966

Dear Jim,

I have tried in the accompanying note to summarize the more important points of our discussion on October 25th. Your comments are invited. If you have any additions to the list at the end please let me know; I should also like an indication of which of these suggestions you consider the most worthy of research.

Yours sincerely,

Kappa

Enclosure + copy of
memo for discussion.

Dr. J. Lovelock,
BOWERCHALKE,
Nr. Salisbury,
Wilts.

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DISCUSSION ON POSSIBLE USES OF METHANE OTHER THAN FOR PROTEIN, FERTILIZERS AND FUEL.

SHELL CENTRE, OCTOBER 25TH, 1966.

Participants: Professor D.H.R. Barton
Professor J. W. Cornforth
Dr. R. H. Jaeger
Professor G. Popják
Professor T. M. Sugden

It was agreed to base the discussion on the memorandum presented by Professor Cornforth.

The first point discussed was the proportion of North Sea methane which could be available as a chemical feedstock. All felt strongly that it would be a great pity to waste the great bulk of this methane by burning it as fuel. A question which remained unanswered was whether a large proportion of North Sea methane could be diverted for use a chemical feedstock by paying a premium for it (e.g., by buying it back from the Gas Council) and, if so, what this premium might be.

The meeting considered which large-scale chemical uses for methane appeared not to justify further research. These were thought to be

(1) Ethylene

(2) Methanol

(3) Hydrogen cyanide, cyanogen.

Ethylene was thought to be the most important product at which to aim, and the availability of pure methane seemed to make possible the use of less brutal methods of reforming than have been used up to now.

Other possible reactions of methane were suggested, but these can conveniently be considered in the context of the three uses listed above.

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It was thought that ethylene rather than acetylene should be aimed at. The possible disposal of acetylene by polymerizing it to benzene was noted. (Another possibility, not discussed, would be to catalyse combination of acetylene with some of the by-product

hydrogen to give more ethylene). The Hoechst process burns its tail gas in the flame used for cracking the methane, but the hydrogen in this tail gas could be valuable in a refinery if it were pure enough.

Professor Barton presented a family of ideas based on the conversion of methane to methyl radicals or carbenes, followed by syntheses of various types.

(i) A process was imagined in which methane and air (or an equivalent radical generator), together if necessary with an initiator, passed through a first reaction zone and then (if necessary after a preliminary quenching) met an injected stream of a third reagent.

In a process for making ethylene, this third reagent might be sulphur dioxide, which could combined with two carbene molecules to give, first, $CH_2 = SO_2$, then ethylene episulphone, and finally ethylene and sulphur dioxide.

Other third substances envisaged for this type of reactor were:

(a) Carbon monoxide, to give ketene from carbene and acetic acid from methyl radicals.

(b) Phosgene, to give acetyl chloride.

(c) Silicon tetrachloride, to give methylsilane halides.

(d) Boron trichloride, to give methylboron halides.

(e) Alkyl phosphites, to give phosphorus compounds.

(f) Phosphorus, to give phosphorus compounds.

(g) Sulphur, to give sulphur compounds.

(ii) Liquid metals, e.g. metallic sodium, might at high temperatures abstract hydrogen from methane. A possible reaction sequence is:

$$2CH_4 + 4Na \longrightarrow 2NaCH_3 + 2NaH$$

$$2NaCH_3 \longrightarrow C_2H_4 + 2NaH$$

$$4NaH \longrightarrow 4Na + 2H_2$$

A variant of this scheme is to use excited mercury vapour:

$$CH_4 + Hg \longrightarrow CH_3HgH \longrightarrow CH_2 + H_2 + Hg$$

$$2CH_2 \longrightarrow C_2H_4$$

(iii) If methane is first halogenated, cracking of the halogen compound in the presence of more methane or of other gases could

lead to synthesis:

(a) $CH_2Cl_2 \longrightarrow CHCl + HCl$

$CH_4 + CHCl \longrightarrow C_2H_4 + HCl$

(b) $CH_3Cl \longrightarrow CH_2 + HCl$

$CH_2 + CO + HCl \longrightarrow CH_3COCl$.

Methanol It was agreed that a better direct process for oxidation of methane to methanol would be useful, especially for possible utilization of methane in industrially undeveloped countries. Professor Sugden mentioned experiments with methane and singlet oxygen or with atomic oxygen.

It was generally felt that there were possibilities for activating the methane-oxygen reaction at relatively low temperatures, for example by photolysis, silent electrical discharge, or radiation.

The KSLA process for making methanol via methyl chloride from oxychlorination of methane was touched on. Would it be economic with a feedstock of pure methane?

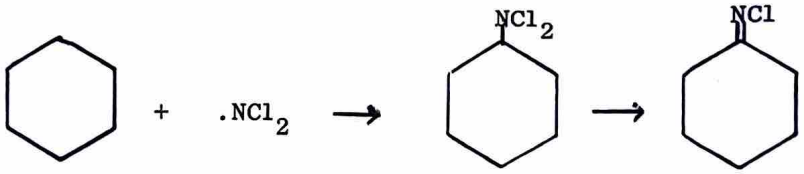
Hydrogen cyanide, cyanogen Preparation of these substances from methane and nitrogen was felt to be the route most worth investigation. Professor Sugden thought that activation of nitrogen in a plasma jet, followed by reaction with methane, might be a more economic proposition than use of plasma jets to prepare, e.g., acetylene. Other activations of nitrogen came into question and the claimed catalytic activity of barium cyanamide for synthesis of hydrogen cyanide or cyanogen from methane and nitrogen was mentioned. If cyanogen were aimed at, it would be for the preparation of oxamide (fertilizer).

The meeting discussed some possibilities of utilizing impure methane in industrially undeveloped countries. Interest was expressed in the reduction of phosphate rock by natural gas to phosphorus, which could be shipped for processing elsewhere. It was recognized that this process needed simultaneous availability of phosphate rock, silica and natural gas in one locality.

Dr. Lovelock in a memorandum to Professor Sugden suggested an industrial complex on the shore of the North Sea, using the simultaneous availability of air, salt water, and cheap methane. Some of the methane would be used to provide electrical power; waste heat from the turbines (and other processes) would serve to concentrate sea water by flash distillation. The fresh water would be sold; the brine used to make chlorine, caustic soda, magnesium, bromine, potash, etc. Some of the chlorine would be utilized for methyl chloride and methanol. An air liquefaction plant would run from off-peak power of the power station (some power from which would be sold to CEGB) and provide oxygen and nitrogen for conversions of methane to methanol, ammonia, ammonium cyanide, higher hydrocarbons.

A "non-chemical" use suggested for methane was as carrier gas in large-scale gas-liquid chromatography.

Professor Barton mentioned, in the course of a discussion on free-radical reactions, that he was attracted by the possibility of using $.NCl_2$ radicals, generated from ammonia and chlorine, for reaction with hydrocarbons. A reaction with cyclohexane might proceed:



Solvolysis of the N—chloroimide would be expected to give caprolactam, the intermediate for Nylon 6.

Suggestions for research on improved utilization of methane

(1) Methane as carrier gas in large-scale gas-liquid chromatography.

(2) Direct oxidation of methane to methanol by oxygen or air.

(3) Activation of methane by conversion into free radicals and carbene, followed by reaction with other molecular species.

(4) Possible production of ethylene by reaction of methane with (i) liquid alkali metals (ii) mercury vapour.

(5) Direct use of methane for hydrodesulphurization of petroleum fractions.

(6) Activation of nitrogen by plasma jet or by other means, followed by reaction with methane.

(7) Pyrolysis of chloromethanes in the presence of methane and of other molecular species.

(8) Reactions of methane and nitrogen leading to cyanogen.

1.11.66

We are to discuss possible uses of methane other than for fuel, protein or fertilizer. This memorandum endeavours to supply background information, to survey existing uses, and to present some suggestions for future development.

This country never had a significant source of indigenous natural gas until now; and the liquefied methane which Shell brings here in relatively small quantity is all mixed with other fuel gas and burned. Now, the Gas Council's chairman (quoted in The Guardian, October 12th, 1966) estimates that the North Sea could yield 10^9 cubic feet of natural gas a day for 30 years, and that this output could rise to four times as much. 10^9 cubic feet of methane (at NTP) weigh 20,000 metric tons: this makes a yearly output of 7.3×10^6 tons — a significant though small fraction of the country's fuel consumption.

All indications are that most of the methane brought ashore — and particularly the gas from the large Shell-Esso field at Leman Bank off Great Yarmouth — will be relatively pure methane, substantially free from other hydrocarbons, from volatile sulphides, and from nitrogen.

Gas is usually priced on the basis of its heat of combustion: so much per therm (1 therm = 10^5 BTU = 25×10^6 cal.). A therm of North Sea gas would weigh about 2 kg. Thus at a price of 1^d per therm (which the Gas Council thinks would give Shell-Esso a wide profit margin!) the price of methane works out around £2 per ton. Prices of this order are well below those of crude oil and they place methane along with a few other materials (water, salt, chalk) as one of the cheapest "pure" chemicals available in Britain.

In some other parts of the world, natural gas is liberated in embarrassingly large quantity at oilfields. Often, practically no use can be made of the methane and ethane left after the gases which can be liquefied by pressure alone have been separated; and the gas is either burned in huge flares or is pumped underground to keep up fluidity and pressure over the oilfield (this is not always possible). Neither course is popular in the countries concerned, but usually they have not the wealth required either to distribute much gas for domestic use or to set up heavy gas-consuming industries; and the oil companies are themselves reluctant to set up manufacturing industries in politically unstable areas, particularly if these require large capital investment. Moreover, natural gas of this type would rarely be pure methane; and any process making use of it would usually have to cope with the presence of other molecular species or with the cost of removing them. And although the gas would for a time be very cheap — cheaper than North Sea gas — to buy in some countries of origin, it would not be very cheap after being transported as liquid to another country for processing.

There are also deposits of natural gas in parts of the world where it remains largely untapped for lack of markets. Much the same economic and political considerations apply to these, except that some of them yield methane of good quality.

In the United States, natural gas has been a fuel and a raw material for several decades. The following figures, taken from Chemical and Engineering News, September 6th, 1965, show present-day consumption of natural gas for various major uses in a modern industrial society.

In 1965 the estimated total production of natural gas in the U.S. was about 32×10^7 tons. Almost 98% of this went as fuel. Of the 2.1% which did not (and that fraction, at 7×10^6 tons, equals the total estimated production of North Sea gas!) nearly half was used to make carbon-black and most of the rest went into the manufacture of ammonia for fertilizer. After rapid increases in the post-war years there appears to be no present trend in the U.S. towards large increases in the use of natural gas, and the proportion used as chemical feedstock is not increasing at all.

If the expected output from the North Sea were divided in similar ratio, only 15×10^4 tons a year would be available as chemical feedstock, and perhaps 5×10^4 tons of this for purposes other than manufacture of fertilizer or carbon-black. No other large-scale use would be possible, unless its profitability was such that it could afford to pay a premium over the price of methane used as fuel; or unless, most improbably, national policy deliberately limited the use of methane as fuel.

In undeveloped countries the problems are different. Competition from the fuel-user is much smaller; alternative uses must then be on a large enough scale to justify the tapping of a gas-field, the construction of pipelines etc., and capital investment in manufacturing plant should be kept as low as possible.

In all countries the costs of moving the gas from where it is produced to where it is consumed, and of moving gas-derived products from where they are made to where they are sold have to be considered. For example, the price paid by the Gas Council for Leman Bank gas as it comes ashore would be taken as the "price" of this gas used by Shell or Esso for their own purposes. If the gas had to be piped inland, the additional cost would be about $2\frac{1}{2}$d per ton mile. Thus methane at the end of a hundred-mile inland pipeline would be costed at about £1 per ton above the Gas Council price. Methane delivered ashore as gas after a 5,000-mile journey in liquid form by tanker would cost about £7 per ton more than at the port where it was liquefied, and the cost would not be much less for shorter journeys because most of it is incurred on shore. Substances which are liquid at ordinary temperatures and pressures can be transported by tanker for very much less — (say one-tenth to one-third of the cost for liquid

methane, for short and very long voyages respectively). The cost per ton of moving such liquids by pipeline is also smaller than for piped gas — about one-third. The information on which this paragraph is based was obtained from Shell's Natural Gas function; I have simplified without, I hope, misconstruction.

We might, then, divide the various uses of methane into four categories:

A. Uses allowing production in industrially undeveloped countries and sale (i) locally (ii) abroad.

B. Uses allowing production in industrially developed countries and sale (i) locally (ii) abroad.

Some uses may span more than one category, but the classification seems useful.

We now come to the actual uses, present and potential, of methane, and we may glance first at two of the "forbidden" subjects: protein and fuel. The fermentation of methane is being studied at Milstead with the primary objective of producing edible protein — if possible, for human food. However, autoclaved cultures of methane bacteria are found to be excellent growth media for a wide variety of other micro-organisms. Thus it is possible to imagine methane, at one remove, as the carbon source for some of the products of the fermentation industry — food additives, antibiotics, vitamins, and some others. If these relatively small-volume and relatively valuable products were produced in isolation they would come in category B; if they are auxiliary to a plant producing protein they would probably enter category A(ii) as well.

Again, it has been claimed that greenhouses heated by burning hydrocarbons grow more produce than when steam-heated. Methane could be used for this purpose — a source of heat and of carbon dioxide for growth — and it might be used in incandescent burners to supply light for growth as well. This is a category B(i) use.

Turning now to "permitted" subjects, we can make a first discussion of these into uses where methane is chemically changed and those in which it is not. I can think of only one use in the latter category: methane as a blanket gas for certain industrial processes requiring exclusion of oxygen. This is another category B(i) use and not a large one.

We are left with those uses in which methane is chemically altered. Where these uses are also applicable to other hydrocarbons, methane suffers from the disadvantage of chemical stability: the activation energy for any reaction of methane is higher than that

for the corresponding reaction of any homologue. Against this must be set the advantages that methane can be much cheaper than any other hydrocarbon, and that it has the highest hydrogen content.

I have concluded that all the chemical reactions of methane of potential practical importance can be grouped in four categories:

(1) Reactions with oxygen, oxygen-in-air, or steam

(2) Reactions with nitrogen or ammonia

(3) Reactions with halogens

(4) Thermal or thermal-catalytic dissociation, followed sometimes by recombination of fragments or reaction with other molecular species.

Any further categories which occur to other members could be added to these.

1) Reactions with oxygen, oxygen-in-air or steam. Reactions of these types are already in large-scale use, largely for the synthesis of ammonia, methanol and formaldehyde, sometimes for the production of hydrogen. Manufacture of ammonia is outside our terms of reference. Manufacture of hydrogen from methane and steam is a well-established process and its profitability in a particular environment is now a matter of economics. However, methane which could be used for this purpose without pre-purification, and which needed to be piped only a short distance to an oil refinery, seems rather attractive as a source of hydrogen for hydro-treating and hydrodesulphurization. Refineries which had to take 1% by weight of sulphur out of ten million tons of crude a year would need about 2.5×10^4 tons of hydrogen. If the heat required for the methane-steam reaction is generated from a petroleum fraction, this means an annual consumption of at least 5×10^4 tons of methane; more, if some methane is burned to provide the heat. This would be a category B(i) use and a major one for this country. At present, the platformer at a refinery can generally produce all the hydrogen needed, very cheaply; but the time is foreseen when clean-air regulations will compel hydro-desulphurization of a much larger proportion of crude than at present, when demand for hydrogen for this purpose and for other forms of hydrotreating may outrun the supply from platforming. We shall return later to this problem.

Most of the methanol synthesized from natural gas is made by combination of methane with a limited amount of oxygen to give a carbon-monoxide-hydrogen mixture which is passed over a catalyst to produce methanol; nearly all the formaldehyde is made from methanol by dehydrogenation.

Processes are also known for direct oxidation of methane to methanol and formaldehyde. It is difficult to assess how much

effort has gone into this approach; most of the work has probably never been disclosed. However, it does seem that although the two-step synthesis of methanol from natural gas is at present more efficient, its capital requirements are probably intrinsically higher. Production of methanol and formaldehyde are now category B uses. It seems worth while to glance at the possibilities of moving them into category A.

A major obstacle to the economic progress of some undeveloped regions, for example in the Middle East and India, is the lack of a cheap, easily portable, easy-to-store fuel which can be burned in simple apparatus. For want of this, vegetation which could resist soil erosion is stripped from the land to feed fires, and dung which could raise the fertility of the soil is dried and burned. The income of the average family is so low that only an extremely cheap fuel would be bought. I wonder whether methanol could become such a fuel. In a country where natural gas is either remaining untapped or is being flared, a direct oxidation process producing methanol from natural gas at the site of gas production could probably afford to be wasteful of methane, and might not require too much capital. The product would yield on burning only 40% of the heat energy of the same weight of methane, but for heat content it is better than dry wood and much better than dry dung. The effects of drinking it unmixed with its homologue are so prompt and unpleasant that addiction would be unlikely. It is easy to transport, to store, and to burn for fuel. A local government might be ready to subsidize manufacture to some extent; especially a government which drew oil revenues. Surplus production could be transported oversea at low cost, and it might find an expanding market. Developments in electrical accumulators, especially the sodium-sulphur cell recently disclosed, suggest that competition from electrically powered cars, silent and fume-free, may increase; one possible answer is a car powered by fuel cells running on methanol. All this is, of course, highly speculative and dependent on a cheap process being developed.

2) Reactions with nitrogen or ammonia. Processes for reaction of methane with ammonia to yield hydrogen cyanide have been in operation for some time and are a major source of hydrogen cyanide, production of which in the U.S. currently runs at some 2×10^5 tons a year. Most of it now goes into acrylonitrile and methyl methacrylate; but the propylene-ammonia-air process for acrylonitrile produces hydrogen cyanide, instead of consuming it as earlier processes do, so that demand for hydrogen cyanide from methane may slacken. These processes are obviously a category B use for methane.

Some work has been done, and at one time seems to have extended to manufacture, on the reaction between methane and nitrogen to give hydrogen cyanide or cyanogen. It is at present a difficult process and not much work seems to have been done with it in recent years; but there are several variants and it is a reaction which might

conceivably attain category A. The objective would be to produce, not hydrogen cyanide, but oxamide via cyanogen. Oxamide is a slow-release nitrogenous fertilizer. An analogous process is the formation of hydrogen cyanide from methane and nitric oxide. All these reactions of methane are high-temperature processes.

3) Reactions with halogens. Quite a number of halogenated methanes are sold in commercial quantities: all four chloro-derivatives, methyl bromide and methyl chlorobromide, and the chlorofluoro derivatives. Reaction of methane with chlorine in the presence of air and of the Shell catalyst which promotes re-oxidation of hydrogen chloride to chlorine has been studied at KSLA. With pure methane, methyl chloride and a little methylene chloride are produced readily, and can be hydrolysed by steam to give methanol with a little formaldehyde, and hydrogen chloride which is returned to the process. If the methane contains higher homologues, they are chlorinated much faster and this tends to upset the balance of the process. Nevertheless, this might be a category A use where pure methane can be supplied. Shell are not at present manufacturers of chlorine or of hydrogen chloride and while this situation remains we are unlikely to manufacture chlorinated methanes for sale.

4) Thermal or thermal-catalytic dissociation, followed sometimes by recombination of fragments or reaction with other molecular species.

The simplest-looking thermal dissociation of methane is to carbon and hydrogen:

$$CH_4 \longrightarrow C + 2H_2$$

When this is done by passing methane over white-hot silica, complete decomposition of methane is not achieved; about 50% of reacted methane goes to hydrocarbons, so that the process is not a source of pure hydrogen; and the carbon-black produced is undesirably coarse in grain. If carbon-black is desired, partial combustion is better.

Other pyrolyses of methane have been aimed at acetylene and ethylene. A Hoechst process cracks methane to ethylene, acetylene and hydrogen. It seems possible that an oil refinery might be interested in a similar process if the acetylene were subsequently polymerized (as can be done catalytically) to benzene. Ethylene is useful at a refinery for several purposes; and the residual hydrogen, if pure enough, could be used for hydrodesulphurization. In theory, such a process would yield about three times as much hydrogen per ton of benzene as would a platformer. As discussed earlier, the demand for hydrogen at refineries is quite likely in the future to rise faster than the demand for aromatics.

This is a somewhat roundabout method for using methane as a source of hydrogen; are more direct methods possible? Concentrating still upon hydrodesulphurization, I wonder if any catalyst would selectively mobilize the hydrogen of methane dissolved under pressure in the petroleum fraction which is being treated. The catalytic decomposition of methane gives hydrogen and a number of chemically reactive one-carbon fragments which might possibly react (e.g. by bond insertion) with the other hydrocarbons present. Ideally, one could get hydrodesulphurization and at the same time about 1% more oil for each 1% of sulphur removed. Possible snags are manifold — e.g., a high concentration of free hydrogen is probably required, and this would slow down the decomposition of methane — but the potential reward is large and perhaps worth a closer look at the process. A little methane appears to be produced in the present process for hydrodesulphurization — is it in equilibrium with hydrogen?

All the processes discussed so far in this section are category B. The only possibility I can see for a category A process of the type is the polymerization of methane with a limited amount of oxygen to give higher hydrocarbons and water. In principle this can already be done by burning methane to carbon monoxide and hydrogen, and combining these over a Fischer-Tropsch catalyst. The capital cost of this process is probably too high for category A, but if the two stages, or something equivalent to them, could be combined the capital cost might become low enough.

I shall conclude by grouping the suggestions made above and thus providing a framework for adding suggestions by other members.

1) Reactions with oxygen, oxygen-in-air, or steam

(i) Steam reforming for hydrogen production

(ii) Direct oxidation of methane to methanol.

2) Reactions with nitrogen or ammonia

(i) Hydrogen cyanide (ammonia)

(ii) Hydrogen cyanide or cyanogen (nitrogen)

3) Reactions with halogens

(i) KSLA methanol process.

4) Thermal or thermal-catalytic dissociation, followed sometimes by recombination of fragments or reaction with other molecular species.

(i) Carbon-black

(ii) Ethylene-benzene-hydrogen

(iii) Catalytic desulphurization of petroleum

(iv) Polymerization-oxidation to higher hydrocarbons.

18th October, 1966