# The dehydrogenative coupling of methane to form higher hydrocarbons in a hot wire thermal diffusion column

Hyman D. Gesser and Lawrence A. Morton
*Dept. of Chemistry, University of Manitoba, Winnipeg, Manitoba, Canada, R3T 2N2*

Received 25 June 1991; accepted 5 November 1991

The dehydrogenative coupling of methane in a hot wire thermal diffusion column (TDC) produced higher hydrocarbons separated and identified by GCMS; this novel method shows good promise (30%+ conversion) for the utilisation of natural gas to produce gasoline.

**Keywords:** Methane coupling; methane to higher hydrocarbons reaction in thermal diffusion column

The thermal polymerisation of methane, in which methane was passed through a heated tube (porcelain or quartz at 1050°C) to yield 18% conversion to condensed hydrocarbons, was reported by Fischer [1] in 1928. Various approaches were taken to improve the yield with little success.

Later, however Hirota [2] utilised a thermal diffusion column (TDC), invented by Clusius and Dickel [3], to study the reaction. This had the effect of thermally separating the hydrogen of reaction from the free radicals and ensuing hydrocarbons formed, when methane was passed upward through the TDC.

$$CH_4 \rightarrow H_2 + \text{Free radicals } (nCH_3)$$

$$n(CH_x) \rightarrow C_nH_{nx}.$$

The TDC consisted of an electrically heated wire (tungsten) centrally suspended in a glass diffusion column. The free radicals formed at the wire produced hydrocarbons which condensed on the cold wall of the TDC.

Using this technique Hirota improved the conversion of the methane to a maximum of 42%, at a wire temperature of 1300°C and a cold wall temperature of 30°C. The liquid product was described as aromatic and the solid as naphthalenic.

This early work was reinvestigated by Yamaguchi and coworkers [4]. In addition to confirming Hirota's findings these authors interestingly discovered

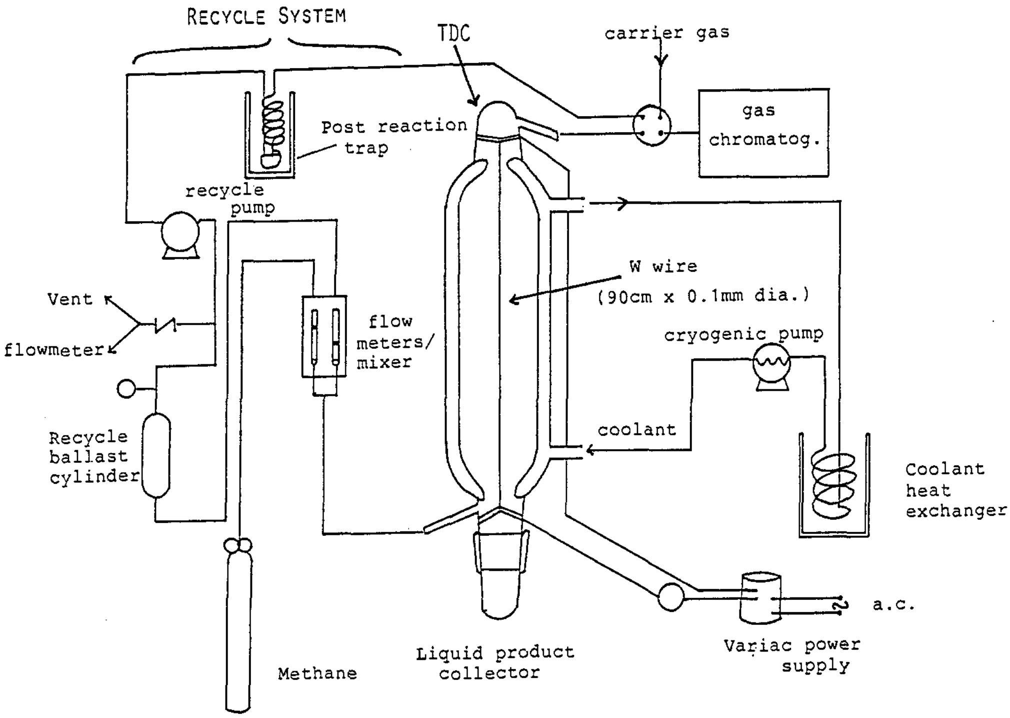

Fig. 1. The thermal diffusion column (TDC) and recycle system.

that when the TDC was operated with methane flowing downwards, under the same conditions, the predominant product was ethylene, maximising at 91.5% selectivity at a conversion of 9.4% and a wire temperature of 1200°C, consuming 450 W. The same authors had stated previously that analysis of the liquid product was not performed [5].

It is the purpose of this communication to describe the work carried out to identify and quantify the compounds in the hydrocarbon polymerisation product and to increase its aliphatic content.

A feed of pure methane with 4.5% added $N_2$ was passed through a glass thermal diffusion column, 23 mm I.D. (figure 1). Delivered at atmospheric pressure, the methane was fed upwards through the TDC, maintained at a flow rate of 30 mL/min or 1.8 L/hour, similar to the Japanese studies.

Prior to the introduction of the methane the apparatus was purged with nitrogen to flush air out of the system. An electrical current sufficient to achieve a wire temperature of between 800–900°C (determined by optical pyrometer) was provided from a variable autotransformer (capacity–140VAC, 20A), operating usually around 2.5 A at 126 V using a 1 m length tungsten wire 0.1 mm in diameter. The effluent product stream was analyzed by on-line gas chromatography (Varian 1800–FID., Porapak Q–10′ × 1.8″ o.d SS and DB-5 Megabore capillary–15 m × 0.52 mm; 1.5 $\mu$m coating–J&W). The condensed liquid product and the gas effluent were analysed subsequently by GC-mass spectroscopy. Two instruments were used: A VG 11-250J coupled to a Hewlett Packard 5890 gas chromatograph and Finnigan Ion Trap 800–Varian 3400 combination. Both GCMS chromatographs equipped with DB-5 capillary columns (30 m × 0.26 mm., 0.25 $\mu$m coating).

The liquid product was too viscous to flow by gravity and so it was washed down the TDC walls using acetone. The solvent was subsequently removed by evaporation but added again to prepare a quantitative solution for analysis.

The GC analysis of the oil is shown in fig. 2. In GC/MS analysis the Mass Spectrometer filament was turned on only after the solvent peak was deamed to have passed through the ionization chamber.

Three separate studies were carried out. In the first the TDC was operated at a wire temperature of 880°C and a wall temperature of 15°C (water coolant) in the single pass mode. The on-line analysis of the effluent gas indicated $C_2$-$C_6$ hydrocarbons, including ethylene (confirmed) which decreased with reaction time. The collected product was a viscous, dark brown naphthelenic mixture containing some solid material. A qualitative analysis of this product is given in table 1.

In the second study, in an effort to preserve the aliphatic hydrocarbons, the TDC walls were cooled with chilled ethanol, affording a wall temperature of −20°C under reaction conditions. This had the effect of increasing both the wire-wall temperature gradient and the product condensation rate (thermal diffusion effect), while limiting the subsequent thermal dehydrogenation and radical interaction of the primary compounds. The collected product (table 2) was still brown and viscous, but with no solid content, and analysis indicated the presence of some aliphatic hydrocarbons.

In a continuing effort to preserve the primary products, a recycle system was devised to incorporate the TDC and recirculate some of the unreacted lighter hydrocarbons and product hydrogen with fresh methane feed. It was anticipated that the presence of hydrogen in the methane feed would displace the radical combination to unsaturates and hydrogen equilibrium in favour of the saturated primary product by limiting the dehydrogenation of the primary saturates and by hydrogenating the secondary unsaturates. This system required the addition of a recirculating pump (Metal Bellows Co., -MB 155), a pressure switch, ballast (recycle gas) storage tank, cold trap (−78°C) and a methane/recycle gas control and mixing facility (fig. 1). As in the previous study the TDC was cooled with chilled ethanol, though the temperature of the system was reduced to −30°C to −40°C through improved insulation. The results show (table 3) that compounds with chain lengths longer than $C_6$ were produced. This addressed the question as to whether chain building continued beyond $C_6$ or not and that subsequent dehydrogenation/aromatization followed by aromatic–aromatic and aromatic–radical interactions would then predominate. The results of this study show that relatively long hydrocarbon chains are formed in the radical reactions and that

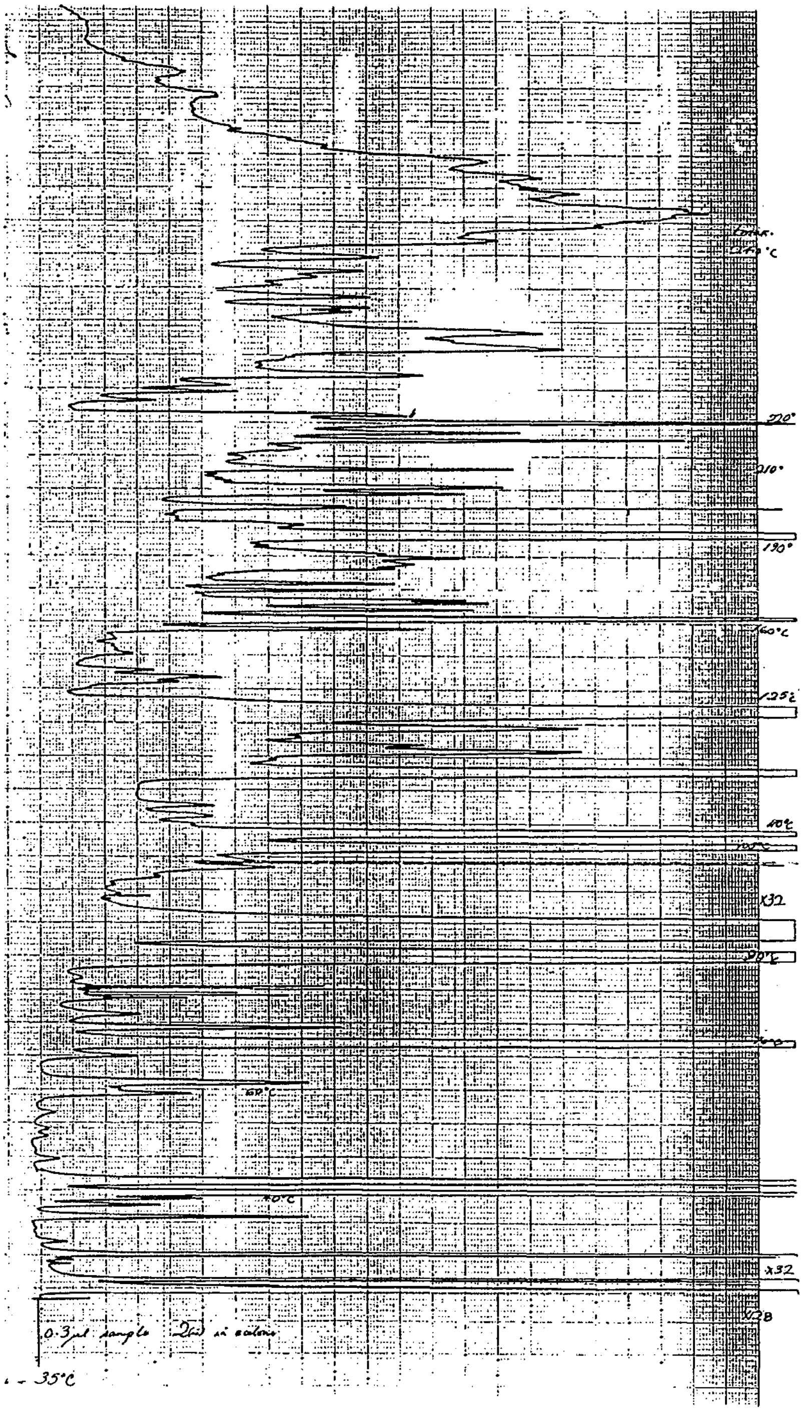

Fig. 2. G.C. analysis of the acetone/oil solution. Temperature programmed.

Table 1
GCMS analysis of collected liquid sample from the thermal decoupling of $CH_4$ at 880°C wire temp. (W–0.1 mm dia.) and 30 mL/min $CH_4$–TDC wall temp. = 15°C

| Scan time | Compound | Purity (MS) |
|---|---|---|
| 20 | 1,3 dimethylbenzene | 93.5 |
| 23 | ethylbenzene | 95.5 |
| 81 | bicyclo[4.2.0]-1,3,5-triene | 91.7 |
|  | 1,3,5,7-cyclooctatetraene | 89.7 |
| 180 | 1 H-indene | 94.9 |
|  | 1-propynylbenzene | 93.8 |
| 282 | 1-cyclohexenylbenzene | 75.1 |
| 288 | naphthalene | 96.3 |
| 311 | azulene | 80.3 |
| 408 | 1-methylnaphthalene | 96.2 |
| 426 | 2-methylnaphthalene | 94.1 |
| 483 | 2-ethylnaphthalene | 97.1 |
| 513 | acenonaphthene | 94.8 |
| 527 | 1,1-biphenyl | 95.6 |
| 542 | acenaphthalene | 92.9 |
| 630 | 1H-phenalene | 94.6 |
| 643 | 9H-fluorene | 93.9 |
| 656 | 2-methyl-9H-fluorene | 90.4 |

Analysis carried out using VG 11-250-J/HP 5890 MS-GC combination, incorporating DB-5 capillary column (30×0.25 mm i.d.–Supelco).

Table 2
GCMS analysis of collected liquid sample from the thermal decoupling of $CH_4$ at 880°C wire temp. (W–0.1 mm dia.) and 30 mL/min $CH_4$-TDC wall temp. = −20°C

| Scan time | Compound | Purity (MS) |
|---|---|---|
| 24 | 1-buten-3-yne | 51.2 |
| 28 | 1-penten-3-yne | 94.5 |
| 30 | 2,4-hexadiyne | 82.2 |
| 47 | 1,3-hexadien-5-yne | 94.5 |
| 54 | methylbenzene | 92.7 |
| 63 | 1,5-heptadiene-3-yne | 86.4 |
| 77 | 1,3,5-cycloheptatriene | 92.4 |
| 99 | ethynylbenzene | 97.4 |
|  | bicyclo[4.2.0]octa-1,3,5-triene | 94.2 |
|  | 1,3,5,7-cyclooctatetraene | 92.7 |
| 264 | 1H-indene | 96.0 |
| 395 | naphthalene | 95.8 |
| 469 | 1,1-biphenyl | 90.1 |
| 568 | 9H-fluorene | 93.8 |
| 603 | 9-methyl-9H-fluorene | 93.8 |
| 662 | phenanthrene | 94.7 |

Analysis carried out using Finnigan Mat Ion Trap 800–Varian 3400 DB-5 Megabore capillary column (15 mm×0.52 mm i.d. J&W).

Table 3
GCMS analysis of collected liquid product from the thermal decoupling of $CH_4$ at 850°C wire temp. (W–0.1 mm dia.) and 30 mL/min $CH_4$, 10 mL/min recycle gas TDC wall temp = −35°C

| Scan time | Compound | % Purity (MS) | % Amount |
|---|---|---|---|
| 120 | 3-penten-1-yne | 86.6 | 0.2 |
| 134 | 1,3-cyclopentadiene | 75.5 | 0.2 |
| 148 | 1,3-hexadien-5-yne | 88.3 | 0.1 |
| 170 | 2-hexene-4-yne | 81.3 | 0.7 |
| 173 | 1,3,5-hexatriene | 85.1 | 0.4 |
| 188 | benzene | 59.7 | 16.3 |
| 191 | 1,3 & 1,5-hexadiene-3-yne | 53.2 | 23.1 |
| 193 | 1,3-cyclohexadiene | 79.6 | 11.7 |
| 197 | 1,4-cyclohexadiene | 87.9 | 0.2 |
| 361 | 1,5-heptadiene-3-yne | 73.6 | 18.0 |
| 430 | 2,3,4-trimethyl hexane | 71.1 | 7.9 |
| 538 | 5-(1-methylethylidene)-1,3-cyclopentadiene | 81.6 | 1.0 |
| 554 | 1,3-dimethylbenzene | 85.2 | 1.2 |
| 566 | ethynylbenzene | 75.2 | 1.5 |
| 592 | 3-cyclohexene-1-yl-benzene | 65.2 | 4.0 |
| 712 | 3-ethyloctane | 74.6 | 0.1 |
| 753 | undecane | 80.7 | 6.5 |
| 973 | naphthalene | 92.8 | 1.6 |
| 1085 | 1-ethylidene-1H-indene | 87.8 | 0.3 |
| 1101 | 1,4-dihydromethanonaphthalene | 90.0 | 0.3 |
| 1163 | 1,1-biphenyl | 87.7 | 0.2 |
| 1230 | biphenylene | 87.7 | 0.3 |
| 1502 | heptadecane | 71.1 | 4.7 |

Analysis carried out using Finnigan Ion Trap 800-Varian 3400 GCMS.

the reactor conditions, particularly in respect of wire and wall temperature, and hydrogen concentration strongly influence the direction and product composition of the reaction. Conversion of the methane feed was estimated to be 30% based on the change in $CH_4/N_2$ ratio before and after reaction. The products of this study were semiquantitatively estimated by GC peak integration indicating the product distribution under these conditions.

The gaseous products showed only a small decrease in yield as the wall temperatures decreased.

The non-reproducibility of the retention times (scan time) in tables 2 and 3 is due to differences in temperature programming rates of the GC column. The purity refers to the matching efficiency of the sample mass spectrum with that of a library spectrum. In some cases it was not possible to distinguish between isomers because of the small differences in the match (Purity).

The thermal decoupling of methane is dominated by free radicals (in particular methyl radical) reactions followed by subsequent dehydrogenation and cyclization/aromatization. The tungsten wire evidently is instrumental in initiating this process and the wire temperature and TDC thermal gradients (radial and longitudinal) influence the degree of product polymerization. An X-ray diffraction analysis of the wire showed only the additional formation of tungsten carbide.

## Acknowledgement

Financial Support for a research grant from EMR and NSERC is gratefully acknowledged.

## References

[1] F. Fischer, Brennstoff Chem. 9 (1921) 308.
[2] K. Hirota, Bull. Chem. Soc. Jpn. 16(8) (1941) 274.
[3] K. Clusius and G. Dickel, Naturwis. 26 (1938) 546.
[4] J. Yamaguchi and C. Saito, Bull. Chem. Soc. Jpn. 61 (1989) 2649.
[5] J. Yamaguchi, A. Kadota and C. Saito, Chem. Lett. Chem. Soc. Jpn. (1988) 681.