Gaseous hydrocarbons generated during pyrolysis of petroleum source rocks using unconventional grain-size: implications for natural gas composition

Sedat İnan *

TU俾TAK Marmara Research Centre, Earth Sciences Research Institute, Gebze-Kocaeli 41470, Turkey

Abstract

Open-system pyrolysis experiments were performed on a suite of immature to marginally mature source rocks to investigate the influence of kerogen type on primary gas composition and the effect of grain size on gas expulsion characteristics. The pyrolysis of rock powders confirmed that hydrogen-rich kerogens yielded wetter gases than did hydrogen-poor kerogens. Gases detected from the pyrolysis of rock chips were drier than those from powders of equivalent samples. This was due to two processes: the retention and secondary cracking of higher molecular weight pyrolysis products and the preferential expulsion of methane from the rock matrix. These two effects, one chemical the other physical, could be distinguished using a novel approach involving multi-step pyrolysis of rock chips followed by on-line crushing of the residues. The enrichment of methane in natural gas attributed, by earlier workers, to be a consequence of fractionation during secondary migration (post-expulsion) has been proven to be real also during expulsion from source rocks at least for pyrolysis conditions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Natural gas composition; Retention; Secondary cracking; Expulsion; Migration fractionation; Gaseous hydrocarbons; Gas dryness; Pyrolysis; Open system; Restricted system; Unconventional grain size

1. Introduction

It is well known that natural gas of thermogenic origin is much drier (containing more methane) than the gas generated during artificial maturation (pyrolysis) of immature source rocks in open systems (Horsfield et al., 1992; Mango, 1992, 1996; Rice, 1993; Price and Schoell, 1995; Schaefer et al., 1999). Although closed-system pyrolysis generates drier gas (Horsfield et al., 1992; Behar et al., 1995, 1997; Boreham et al., 1999) due to recondensation and aromatisation of the products, its applicability to the natural system implies that source rocks in nature are closed systems. While methane content of natural gas is generally more than 80% by weight, the methane content of gas generated from source rocks during open-anhydrous or closed and water-wet pyrolysis is significantly less and does not exceed 60% by weight (Mango et al., 1994; Price and Schoell, 1995, and references therein). Although this discrepancy in chemical composition of gas generated in laboratory and that of natural gas may have several reasons related to the differences in scale of the two system and their consequent operating mechanisms, Mango and his co-workers concluded that natural gas formation is catalytic, promoted by transition metals, in nature and cannot be duplicated by pyrolysis (Mango, 1992, 1996; Mango et al., 1994). On the other hand, Price and Schoell (1995) have argued that natural gas becomes drier (enriched in methane) through fractionation during secondary migration (post-expulsion) because gases contained in the source rocks are rich in wet (C₂–C₄) components.

It is a proven fact that the chemical composition of gas to be generated from source rocks upon maturation either in laboratory or in natural settings depends on type of kerogen contained and the maturity of source rock (Galimov, 1988; Schoell, 1988; Andresen et al., 1995; Behar et al., 1995; Price and Schoell, 1995; Clayton,
The more hydrogen-rich the kerogen, the wetter the gas it will generate upon maturation and the higher stage of maturity of the source rock the drier the gas it will generate. Following the suggestion of Price and Schoell (1995) alone, it might be argued that the wetter the gas expelled from its source rock, the greater secondary migration distance would be required for methane-rich gas accumulations. In addition to migrational fractionation, there are several natural processes that may lead to dry gas accumulations. To mention just a few of these mechanisms, high solubility of methane in water and its dissolution at lower pressure and temperature conditions (Galimov, 1988; Rice, 1993; Weishauptova and Medek, 1998; Cramer et al., 1999; Schaefer et al., 1999, among many others), mixing of secondary biogenic gas with original reservoir gas (Rice, Schaefer et al., 1999, and references therein). Results of coal desorption experiments show that headspace gas is drier than associated gas obtained after crushing and thermal activation of coal (Rice et al., 1988; Rice, 1993; Krooss, 1988; Whiticar, 1996) are all possible processes contributing to occurrences of methane-rich natural gas accumulations. Therefore, any comparison between chemical compositions of natural and artificially generated gases should take into account the possible effects of the above-mentioned processes.

Among possible contributing processes, the phenomenon of retention of C2–C4 in and/or preferential expulsion of methane from coals speculated by earlier workers (Rice, 1993, and references therein) could be tested for other lithologies in laboratory conditions. Coals are major source and reservoirs for natural gas and thus coalbed gas studies are numerous (Rice, 1993; Clayton, 1998, and references therein). Results of coal desorption experiments show that headspace gas is drier than associated gas obtained after crushing and thermal activation of coal (Rice et al., 1988; Rice, 1993). This suggests that wet gas (C2–C4) components are strongly sorbed to coal surfaces than is methane (Rice, 1993). These experimental results may be taken to suggest that fractionation during gas expulsion is, in addition to the abovementioned processes, a possible contributer to dry natural gas accumulations. Inan et al. (1998) showed that fractionation during expulsion influences gas/oil ratios (GOR) of the pyrolysis products. Whether, the chemical composition of the expelled gas is also affected by this process is yet unknown but it is worth an investigation.

To investigate the possible effects of fractionation during expulsion on chemical composition of generated gas in laboratory experimentations, a suitable analytical set-up is necessary. Conventional open- or closed-system pyrolysis (hydrous or anhydrous) on powder samples is not suitable for this investigation because in this finely-ground state (<250 μm is commonly used), original petrophysical characteristics of the source rock sample is altered. Expulsion of hydrocarbons from source rock is controlled by two consecutive processes, namely the release of hydrocarbons from kerogen, and the movement (primary migration) of these hydrocarbons within the source rock (Pepper and Corvi, 1995, and references therein). In pyrolysis of finely-ground source rocks, the porosity and texture of the source rocks are altered, thus it becomes very difficult, if not impossible, to make any meaningful evaluation of the primary migration effect. Inan et al. (1998) employed both powder (<0.106 mm) and chip (up to 8 mm) splits of a suite of samples in open-system pyrolysis and noted significant differences in efficiency of primary migration of generated hydrocarbons between powder and chip splits of the very same samples.

The aims of this study were (1) to investigate the cause(s) of variations in composition of gases generated and expelled upon pyrolysis of immature to marginally mature source rocks, (2) to delineate the mechanism(s) controlling the chemical composition of gas generated and expelled from a given source rock, (3) to test “the hypothesis that gas fractionation during expulsion leads to drier gas”, and (4) to draw conclusions concerning occurrences of methane-rich natural gas.

2. Samples and experimental methods

2.1. Pyrolysis

For simulation of gas generation and expulsion from source rocks in natural settings, pyrolysis conditions to be used are extremely important. In order to utilise the best available pyrolysis conditions, understanding of how source rocks behave in their natural settings is critical. While some workers have considered source rocks as open-chemical systems (Cooles et al., 1986; Leythaeuser et al., 1987; Durand, 1988; Ungerer, 1990), others have argued that source rocks in nature must resemble closed chemical system (Behar et al., 1995, 1997; Price, 1997a,b). In terms of primary migration of hydrocarbons from source rocks, assuming an open system implies efficient migration, whereas, closed system implies retention and destruction of generated hydrocarbons (Price, 1997b). Although both views on behaviour of source rock as being chemically open- and closed-system have strong merits, it is more likely that source rocks during their evolutions in their natural settings are restricted “neither fully-open nor fully-closed” systems; otherwise, hydrocarbon expulsion from generation site could not take place.

For a successful simulation of hydrocarbon generation and expulsion from source rocks in their natural setting, the pyrolysis conditions should provide restricted, neither fully-open nor fully-closed, environment.
Available pyrolysis techniques are either open or closed systems and either one has advantages and disadvantages compared to the other (Horsfield et al., 1989; Lewan, 1994; Behar et al., 1995, 1997; Burnham, 1995; Horsfield, 1997; Schenk and Horsfield, 1998). The most important shortcomings of both systems is probably the use of powder samples which deviates the experimental conditions from natural conditions in terms of scale of the system (İnan et al., 1998; İnan and Schenk, 2000). Neither open- nor closed-system pyrolysis duplicates natural maturation especially for humic kerogen (Schenk and Horsfield, 1998). On the other hand, neither hydrous closed-system pyrolysis nor anhydrous open-system pyrolysis represent natural source rocks in nature (Lewan, 1994; Horsfield, 1997).

The relatively restricted pyrolysis conditions (İnan et al., 1998; İnan and Horsfield, 2000; İnan and Schenk, 2000) seems to be the closest available system to natural settings. In this technique, coarse grain-size (chip) samples are pyrolysed in an open system. Pyrolysing chip sample has its advantages. On one hand, chip samples impose some restriction on the movements of generated hydrocarbons, on the other, an open system efficiently sweeps the products away from the pyrolysis furnace and prevents further cracking. Moreover, we believe that the release of hydrogen as molecular hydrogen instead of reacting to produce methane (Behar et al., 1995; Horsfield, 1997) is partially eliminated in this system. In this study, we employed chip samples in open-system pyrolysis which we believe is more representative of the restricted natural setting, that is neither fully-open nor fully-closed. Moreover, we conducted pyrolysis with identical conditions on powder splits of the very same samples to determine the differences between the two.

2.2. Samples

A suit of immature to marginally mature samples varying in lithology from limestone to humic coal formed the basis of the investigation (Table 1). A wide range in kerogen type (indicated by HI values in Table 1) is represented. Detailed information on the samples has been given by İnan et al. (1998). For each sample, two different grain-size splits; namely, powder (<0.106 mm) and chip (1–4 mm), were made in order to examine cracking and retention phenomena under open-system pyrolysis conditions.

2.3. Pyrolysis on-line gas chromatographic methods

Three open-system pyrolysis gas chromatographic (Py-GC) methods were used.

2.3.1. Single-step open-system Py-GC

Approximately 5 mg of sample (powder and chip) was placed into the central part of a glass tube (26 mm long; inner sleeve diameter 3 mm). The remaining volume was filled with cleaned quartz wool (see Horsfield et al. (1989) for configuration and experimental details). After thermovaporization of the sample at 300 °C (10 min) to remove volatile material, the sample was pyrolyzed using programmed heating from 300 to 600 °C at 50 °C/min. During pyrolysis a constant flow of helium (50 ml/min) was maintained in order to transport all pyrolysis products to an outside cold trap. At the completion of pyrolysis, the cold-trap was cryogenically heated up to 300 °C and products were swept into and separated by on-line gas chromatography. An HP-1 column (25 m length, 0.32 mm id, and 0.5 μm film thickness) connected to a flame ionization detector was used with helium as carrier gas. The GC oven was programmed from −10 °C (2 min isothermal) to 320 °C at 8 °C/min. Quantification was performed using n-butane as an external standard.

2.3.2. Stepwise open-system Py-GC

Approximately 200 mg of powder and chip splits of the selected marl sample (E43460 and E43463 in Table 1) were pyrolyzed stepwise with a heating rate of 10 °C/min from 300°C to eight end temperatures (between 425 and 600°C at temperature steps of 25°C). At the termination of pyrolysis, the cryogenic trap was heated up to 60°C and on-line GC analyses of C₁–C₄ range products were conducted isothermally at 40°C using the column specified above. At the end of each GC analyses the remaining pyrolysates (C₆+) were vented off by heating the trap to 300°C.

2.3.3. Stepwise open system Py-GC followed by on-line crushing

Step-wise Py-GC analyses of powder and chip splits of the selected marl sample (E43460 and E43463) to final temperatures of 425 and 450°C at 10°C/min was followed by cooling the pyrolysis chamber to 300°C. At the termination of pyrolysis, the cryogenic trap was heated up to 60°C and on-line GC analyses of C₁–C₄ range products were conducted isothermally at 40°C using the column specified above. At the end of each GC analysis, the remaining pyrolysates (C₆+) were vented off by heating the trap to 300°C. Then, using the piston of the MSSV injector, we crushed the sample within the pyrolysis chamber in a manner previously utilised for fluid inclusions (Jochum et al., 1994), and performed thermovaporisation GC analyses of C₁–C₄ range products to see if any gases remained in the sample material after the pyrolysis procedure. Here, again approximately 200 mg of sample was pyrolyzed.

3. Results and discussion

In the following, the results will be discussed separately on possible effects of (1) kerogen type, and (2)
grain size on the chemical composition of gases generated and expelled (detected) during open-system non-isothermal Py-GC experiments.

3.1. Effect of kerogen type on chemical composition of the generated gas

Chemical composition of gas to be generated from organic matter (OM) depends mainly on its chemical structure and hydrogen richness or poorness. Drier gas [higher $C_1/(C_1-C_4)$ ratios] are thought to be generated from H-poor OM, whereas, wetter gas [lower $C_1/(C_1-C_4)$ ratios] is generated from H-rich OM (Rice et al., 1988; Schoell, 1988; Rice, 1993; Andresen et al., 1995; Behar et al., 1995; Clayton, 1998; İnan et al., 1998; Schaefer et al., 1999). Maturity level of the organic matter also influences the chemical composition of the gas generated at a given stage; at advanced stage of maturity drier gas is generated (Andresen et al., 1995; Behar et al., 1995).

Py-GC results on both powder and chip splits of source rock samples are given in Table 2. The results clearly show that H-rich kerogen (hydrogen richness is inferred from high hydrogen index values determined from Rock-Eval pyrolysis), regardless of the lithology of its host rock, generates wetter gas, and H-poor kerogen

### Table 1

Total organic carbon, whole-rock pyrolysis, and vitrinite reflectance data on samples selected for Py-GC analyses

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lithology</th>
<th>Locality</th>
<th>TOC</th>
<th>S1</th>
<th>S2</th>
<th>HI</th>
<th>OI</th>
<th>$T_{\text{max}}$</th>
<th>$%R_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E43457</td>
<td>Limestone</td>
<td>South-east Turkey</td>
<td>10.30</td>
<td>4.89</td>
<td>68.53</td>
<td>665</td>
<td>10</td>
<td>421</td>
<td>_.b</td>
</tr>
<tr>
<td>E43463</td>
<td>Marl</td>
<td>South-east Turkey</td>
<td>2.88</td>
<td>1.94</td>
<td>8.16</td>
<td>283</td>
<td>13</td>
<td>443</td>
<td>0.77</td>
</tr>
<tr>
<td>E43485</td>
<td>Torbanite</td>
<td>NSW Australia</td>
<td>68.80</td>
<td>5.48</td>
<td>558.2</td>
<td>811</td>
<td>3</td>
<td>453</td>
<td>0.22</td>
</tr>
<tr>
<td>E43493</td>
<td>Brown coal</td>
<td>VA, Australia</td>
<td>59.70</td>
<td>9.44</td>
<td>77.63</td>
<td>130</td>
<td>66</td>
<td>412</td>
<td>0.27</td>
</tr>
<tr>
<td>E43497</td>
<td>Shale</td>
<td>Luxembourg</td>
<td>7.55</td>
<td>1.04</td>
<td>43.63</td>
<td>578</td>
<td>26</td>
<td>414</td>
<td>_-.b</td>
</tr>
<tr>
<td>E43501</td>
<td>Humic coal</td>
<td>Zonguldak, Turkey</td>
<td>71.80</td>
<td>7.57</td>
<td>160.97</td>
<td>224</td>
<td>2</td>
<td>448</td>
<td>0.78</td>
</tr>
<tr>
<td>E43026</td>
<td>Coal A</td>
<td>Zonguldak, Turkey</td>
<td>71.30</td>
<td>0.3</td>
<td>152.3</td>
<td>214</td>
<td>7</td>
<td>420</td>
<td>0.50</td>
</tr>
<tr>
<td>E32832</td>
<td>Coal B</td>
<td>Zonguldak, Turkey</td>
<td>64.90</td>
<td>1.5</td>
<td>239.9</td>
<td>370</td>
<td>8</td>
<td>423</td>
<td>0.45</td>
</tr>
</tbody>
</table>

*a* TOC, total organic carbon (wt.%) from LECO analyser; S1, mg volatile HCs/g sample from Rock-Eval pyrolysis; S2, mg pyrolysable HCs/g sample from Rock-Eval pyrolysis; HI, hydrogen index (mg HCs/g TOC); OI, oxgen index (mg CO2/g TOC); $T_{\text{max}}$, pyrolysis temperature at which yield is maximum; $\%R_o$, mean vitrinite reflectance in oil.

*b* Not determined.

### Table 2

Resolved pyrolysis products ($\mu$g/sample) and methane content [$C_1/(C_1-C_3)$] of the generated gases for powder and chip splits of samples of varying lithology

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lithology</th>
<th>Grain size</th>
<th>$C_1$</th>
<th>$C_{2-3}$</th>
<th>$C_{6-14}$</th>
<th>$C_{15-32}$</th>
<th>$C_1/(C_1-C_3)$ (%)</th>
<th>n-Alkene/n-alkane ratio</th>
<th>Aromatics HCs ($C_6-C_{14}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E43454</td>
<td>Limestone</td>
<td>Chip (1–4 mm)</td>
<td>1546</td>
<td>4256</td>
<td>8317</td>
<td>2819</td>
<td>27</td>
<td>0.96</td>
<td>16.2</td>
</tr>
<tr>
<td>E43457</td>
<td>Limestone</td>
<td>Powder (&lt;0.106 mm)</td>
<td>1789</td>
<td>5104</td>
<td>9125</td>
<td>3015</td>
<td>26</td>
<td>1.15</td>
<td>15.4</td>
</tr>
<tr>
<td>E43460</td>
<td>Marl</td>
<td>1–4 mm chip</td>
<td>1167</td>
<td>1458</td>
<td>1518</td>
<td>277</td>
<td>45</td>
<td>0.29</td>
<td>22.0</td>
</tr>
<tr>
<td>E43463</td>
<td>Marl</td>
<td>Powder</td>
<td>607</td>
<td>1448</td>
<td>1670</td>
<td>411</td>
<td>30</td>
<td>0.92</td>
<td>18.3</td>
</tr>
<tr>
<td>E43482</td>
<td>Torbanite</td>
<td>1–4 mm chip</td>
<td>7448</td>
<td>31479</td>
<td>70110</td>
<td>40373</td>
<td>19</td>
<td>0.96</td>
<td>5.2</td>
</tr>
<tr>
<td>E43485</td>
<td>Brown coal</td>
<td>Powder</td>
<td>9499</td>
<td>44749</td>
<td>88815</td>
<td>45254</td>
<td>17</td>
<td>1.14</td>
<td>6.0</td>
</tr>
<tr>
<td>E43490</td>
<td>Brown coal</td>
<td>1–4 mm chip</td>
<td>8273</td>
<td>6126</td>
<td>11526</td>
<td>2870</td>
<td>58</td>
<td>0.90</td>
<td>43.0</td>
</tr>
<tr>
<td>E43493</td>
<td>Brown coal</td>
<td>Powder</td>
<td>10027</td>
<td>8714</td>
<td>16372</td>
<td>6334</td>
<td>54</td>
<td>0.88</td>
<td>41.5</td>
</tr>
<tr>
<td>E43494</td>
<td>Shale</td>
<td>1–4 mm chip</td>
<td>1744</td>
<td>4559</td>
<td>7452</td>
<td>1761</td>
<td>27</td>
<td>1.04</td>
<td>17.9</td>
</tr>
<tr>
<td>E43497</td>
<td>Shale</td>
<td>Powder</td>
<td>1429</td>
<td>4075</td>
<td>6180</td>
<td>1345</td>
<td>26</td>
<td>1.16</td>
<td>19.6</td>
</tr>
<tr>
<td>E43498</td>
<td>Humic coal</td>
<td>1–4 mm chip</td>
<td>14885</td>
<td>13002</td>
<td>14441</td>
<td>6693</td>
<td>53</td>
<td>0.74</td>
<td>36.7</td>
</tr>
<tr>
<td>E43501</td>
<td>Humic coal</td>
<td>Powder</td>
<td>22494</td>
<td>17427</td>
<td>18342</td>
<td>8025</td>
<td>56</td>
<td>0.76</td>
<td>38.7</td>
</tr>
<tr>
<td>E30262</td>
<td>Coal A</td>
<td>&lt;0.25 mm</td>
<td>8974</td>
<td>5840</td>
<td>8097</td>
<td>1493</td>
<td>61</td>
<td>0.85</td>
<td>54.5</td>
</tr>
<tr>
<td>E32832</td>
<td>Coal B</td>
<td>&lt;0.25 mm</td>
<td>13110</td>
<td>15830</td>
<td>23060</td>
<td>7545</td>
<td>45</td>
<td>0.96</td>
<td>38.4</td>
</tr>
</tbody>
</table>

*a* Non-isothermal programmed temperature open system pyrolysis (300 to 600°C at 50°C/min).
generates drier gas. Fig. 1 shows a plot of Rock-Eval derived hydrogen index (HI) versus gas dryness for powder splits of samples listed in Table 2. The data strongly support earlier findings on effect of hydrogen richness of kerogen on composition of generated gas (Galimov, 1988; Andresen et al., 1995; Behar et al., 1995; Inan et al., 1998) and shows, as expected, that methane generation from H-rich (type I and II) kerogen contained in torbanite and limestone, and shale is limited and C_2–C_5 range gaseous products dominate; resulting in wet gas [low C_1/(C_1–C_5)] composition. On the other hand, H-poor coal samples containing dominantly type III kerogen generate drier gas (45 to 60 wt.% methane).

Different lithologies generate gases with significant differences in chemical composition (Fig. 1). However, the controlling mechanism on composition of generated gas is not the lithology of the source rock, but the type of organic matter contained. Therefore, difference in composition of generated gas can be expected from two different samples of similar lithology (e.g. coal). For instance, coal B, containing more than 30% liptinite maceral (Inan et al., 1998), generated wetter gas compared to coal A which is liptinite-poor (Fig. 1). Here, both samples are at low stage of maturity (Table 1), therefore, maturity cannot be the reason for the variation in the chemical composition of gases.

Since we used open system pyrolysis (especially on powder sample), secondary cracking is none or very limited (Behar et al., 1997; Horsfield et al., 1992; Horsfield, 1997; Schenk and Horsfield, 1998). Methane content of the gas from H-rich kerogen is limited because side chains in this type of kerogen are also minimal. However, from humic kerogen, where type of bonds are more complex and side chains more abundant (Tissot and Welte, 1984; Hatcher et al., 1988; Mukhopadhyay and Hatcher, 1993), methane generation is more substantial even with lack of secondary cracking of first formed hydrocarbons.

It is important to note that each sample representing different lithology, except one coal sample, produces drier gas from its chip split compared to its powder (Table 2). We attribute this to fractionation by retention and/or preferential expulsion of generated gases facilitated by use of chip samples, and we will discuss this phenomenon in the next section.

3.2. Effect of sample grain size on chemical composition of the expelled gas

Pyrolysis results on conventional (powder) and unconventional (chip) grain-size splits of each source rock sample clearly show that methane content of gases are higher for chip splits (Table 2), regardless of lithology of the sample and the type of kerogen contained. It must be stressed that the relevant differences in gas composition (e.g. methane content) and quantities described are sometimes very small (Table 2), however, the reliability of the pyrolysis system was checked by using small and large quantities of samples. For the purpose of this investigation, no significant changes in gas dryness was seen from repeated pyrolysis runs; thus, the resulting quantities are comparable. Here, it is apparent that pyrolysis of powder samples underestimates the methane content of expelled gases because the role played by the rock fabric during expulsion of methane is eliminated and/or HMW hydrocarbons escape the system before the system reaches cracking.
temperatures. Therefore, the increase in methane content of the gas, obtained by about one order of magnitude increase in grain-size of the very same sample (from <0.106 to 1–4 mm), is very likely to be a consequence of the following two mechanisms: (1) preferential expulsion of methane due to its higher mobility compared to C2+ gases during pyrolysis; and/or (2) retention and cracking of HMW hydrocarbons producing higher methane content.

A lower n-alkene/n-alkane ratio for C12+ hydrocarbons and higher content of aromatic hydrocarbons (HCs) in C6–C14 range total HCs in the pyrolysates from chip splits compared to powder splits (Table 2) indicate retention. During pyrolysis of chip split, it takes longer time for a product to escape and get detected and that enhances recombination and aromatisation reactions (Schenk and Horsfield, 1998). Lower n-alkene/n-alkane ratios obtained for C12+ pyrolysates of the chip split are also indicative of saturation of n-alkenes by hydrogenation facilitated by longer residence time of the pyrolysates within the sample. Moreover, coke formation during pyrolysis (Burnham and Happe, 1984; Lewan, 1994; Horsfield, 1997) may be the cause for lower total pyrolysat yields from chip splits compared to powder. Regardless of the controlling mechanism, retention of C2+ gases or preferential expulsion of methane, it is clear that the larger grain-size of the sample pyrolysed, the drier the gas is expelled.

To investigate further the possible mechanism(s) responsible for drier gas obtained from chip splits of a given sample, we conducted step-wise Py-GC experiments (400 to 600°C, GC analyses every 25°C) on a selected Marl sample. The reasons for selecting the Marl sample for further investigation was (1) because of its low TOC content, using as much as 200 mg sample did not create trap over-load problem, and (2) it produced as much as 15% difference in methane content of the gas generated from its powder and chip splits during single-step pyrolysis (Table 2).

Gaseous products of the step-wise Py-GC analyses are listed in Table 3. Fig. 2 shows a plot of expelled (detected) C1 and C2–C4 components of the gas generated with pyrolysis temperatures. It is worth noting that the amount of C2–C4 generated from the powder is higher than that of the chip up to pyrolysis temperature of 500°C. Thereafter, at higher temperatures the behaviour is reversed. This phenomenon may be explained as follows.

During pyrolysis of the chip, up to 500°C, C2–C4 values are lower compared to powder; indicating partial retention of these compounds (Fig. 2 and Table 3). However, above pyrolysis temperature of 500°C, C2–C4 values are higher for the chip sample compared to powder sample (Fig. 2 and Table 3), clearly indicating greater retention and cracking of HMW hydrocarbons and/or preferential expulsion of methane during chip pyrolysis in comparison to powder pyrolysis.

As far as effect of retention and cracking of HMW HCs is concerned, the increase in cumulative generation and detection of C2–C4 from chip pyrolysis is less than 10% more than that of powder pyrolysis; 1078 and 998 µg/g sample, respectively (Fig. 2 and Table 3). On the other hand, the increase in cumulative methane generation (and detection by FID) from chip sample is about 50% more than that of powder pyrolysis; 1041 and 761 µg/g sample, respectively (Fig. 2 and Table 3). This observation suggests that contribution of retention and cracking of HMW HCs during pyrolysis of chip sample to C2–C4 formation is insignificant, whereas this phenomenon contributes significantly to methane formation.

Another observation form Fig. 2 is that C2–C4 generation is almost complete by pyrolysis temperatures of 575°C, whereas, methane generation is not complete at maximum pyrolysis temperature of 600°C. Undoubtedly, the completion of generation of C2–C4 before methane is related to different reaction kinetics of formation for methane and C2–C4 components; C2–C4 are generated earlier in maturation. Generation of methane still continuing at maximum temperatures of pyrolysis indicates incomplete pyrolysis (Behar et al., 1995). The effect of incomplete pyrolysis may be reduced either by reducing the heating rate of pyrolysis (Jüngten and Klein, 1975) cited in Schaefer et al., 1999; Burnham and Happe, 1984) or by increasing final pyrolysis temperatures (Cramer et al., 1999). Both remedies clearly indicate that drier gas may be obtained upon complete pyrolysis as late methane generation is complete. We observed the positive effect of decreasing heating rate on the dryness of the gas generated. Methane content of gases generated from pyrolysis of chip splits of the Marl

<table>
<thead>
<tr>
<th>Final temperature (°C)</th>
<th>Powder (&lt;0.106 mm)</th>
<th>Chip (1–4 mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C1</td>
<td>C2–C4</td>
</tr>
<tr>
<td>425</td>
<td>13</td>
<td>90</td>
</tr>
<tr>
<td>450</td>
<td>32</td>
<td>132</td>
</tr>
<tr>
<td>475</td>
<td>90</td>
<td>281</td>
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<tr>
<td>500</td>
<td>157</td>
<td>312</td>
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<td>525</td>
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<tr>
<td>550</td>
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<td>37</td>
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<tr>
<td>575</td>
<td>97</td>
<td>7</td>
</tr>
<tr>
<td>600</td>
<td>63</td>
<td>2</td>
</tr>
<tr>
<td>Total</td>
<td>761</td>
<td>998</td>
</tr>
<tr>
<td>C1/(C1–C4) (%)</td>
<td>43</td>
<td>49</td>
</tr>
</tbody>
</table>
sample at 50°C/min (Table 2) and 10°C/min (Table 3) are 45 and 49%, respectively. Similarly, effect of heating rate on dryness of the gas generated during pyrolysis has been recently reported by Boreham et al. (1999, their Table 3).

Preferential expulsion of methane (or retention of C₂–C₄) takes place earlier in maturation (e.g., below 500°C; see Fig. 2). At higher maturation stages, cracking of HMW compounds leads to especially higher methane content of the expelled gas. Fig. 3 shows the variation in dryness of the generated and expelled gas with increasing pyrolysis temperatures (i.e., increasing maturation) for both powder and chip splits of the Marl sample. Instantaneous gas refers to gas generated and expelled from organic matter at a given pyrolysis temperature; whereas, cumulative gas refers to total gas generated from the beginning of pyrolysis up to a given temperature. Instantaneous and cumulative gas composition for powder and chip splits gets drier with increasing pyrolysis temperature (Fig. 3). Instantaneous gas generation and expulsion from chip and powder versus pyrolysis temperatures show that gas expelled from chip is drier up to temperatures of 500°C; clearly indicating that part of the generated C₂–C₄ components are retained (Fig. 3 and Table 3). From the beginning to the final pyrolysis temperatures, the methane content of cumulative gas is lower for powder sample compared to that of chip. At final pyrolysis temperature, almost pure methane is generated and expelled resulting in gas with over 95% methane.

Fig. 2. Gaseous pyrolysates generated and expelled from powder (<0.106 mm) and chip (1–4 mm) splits of the Marl sample (see Table 1) during open-system programmed temperature step-wise pyrolysis (300 to 600°C, 10°C/min).

Fig. 3. Dryness of instantaneous and cumulative gas generated and expelled from powder (<0.106 mm) and chip (1–4 mm) splits of the Marl sample during open-system programmed temperature step-wise pyrolysis (300 to 600°C, 10°C/min).
The implications of these experimental results for natural gas generation and expulsion may be that at early maturation stages the generated gas is wet (rich in C₂–C₄ components), whereas at higher stages increasingly drier gas is generated and expelled. At early maturation stage, retention of C₂–C₄ components is generally an important phenomenon and may lead to expulsion of drier gas compared to generated gas. Immediate conclusion available from these results is that a gas deposit to be sourced from source rocks of advanced maturity will be drier than those from source rocks of less maturity. Moreover, it could be argued that gas to be generated from source rocks at early or main gas generation stage will be wet. At expulsion stage, gas may be fractionated and becomes drier due to preferential expulsion of methane, but in order for the expelled gas to result in dry gas accumulations, further and major fractionation during secondary migration would be required. Source rocks at advanced maturity stage generate dry gas comparable in composition to reservoired natural gas.

Finally to confirm our interpretation that C₂–C₄ compounds are at least partially retained in the sample during pyrolysis, we needed to conduct yet another unconventional pyrolysis-GC analyses.

Thermovaporisation-GC analyses performed after Py-GC followed by on-line crushing of the sample clearly show that no methane (C₁) or C₂–C₄ range compounds are retained in the powder sample after open system pyrolysis (Table 4 and Fig. 4a). On the other hand, thermovaporisation-GC analyses after crushing the chip sample show that significant amount of C₂–C₄ range compounds were retained after Py-GC (Table 4 and Fig. 4b). This is direct proof that C₂–C₄ range compounds are selectively retained, even at temperatures up to 450°C; supporting the preceding assessment based on the results of step-wise Py-GC. The difference in yields of gaseous products of the Marl sample given in Tables 3 and 4 are attributed to (1) the values in Table 3 are derived from step-wise Py-GC with all steps performed on the very same sample, whereas, values in Table 4 are derived from Py-GC of different aliquot of the Marl sample, and (2) two different instruments, one with and one without on-line crushing system, were used. Considering, the different instruments and different aliquot used in these experiments, the methane content of the gas [C₁/(C₁–C₄)%] generated from powder and chip splits in both systems are satisfactorily similar. For instance, methane content [C₁/(C₁–C₄)%] for gases produced at 450°C and listed in Tables 3 and 4 are 20 and 22, respectively, for the powder and 24 and 26, respectively, for the chip.

It is conceivable that fractionation of gas during migration in natural setting may lead to higher methane content of migrating gas (Price and Schoell, 1995). For instance, many workers believe that the widely observed difference in composition of “headspace” and “associated” gas of coals is caused by the very same
mechanism (Rice, 1993, and references therein). By using chip samples (1–4 mm) for pyrolysis in this study, we have shown that preferential expulsion of methane is an effective mechanism leading to drier gas even during pyrolysis at temperatures >300°C. Moreover, a much closer match between gas composition in pyrolysis studies and gas composition of natural gas can be expected, but that may be achieved by pyrolysing still higher grain-size samples, perhaps at centimetre levels. Our search for a solution to technical difficulties encountered in pyrolysing coarse grain-size samples at centimetre levels are continuing. However, applications of the laboratory findings, discussed so far, to field studies have been initiated.

4. Conclusions

It has been verified that composition of gas to be generated from a given source rock depends on the type of kerogen contained in and the thermal maturity stage (early versus advanced) of the source rock. The chemical composition of the expelled gas is controlled by the initial composition of the generated gas and fractionation during expulsion. Methane is expelled more easily compared to heavier hydrocarbon gases (C₂–C₄). Enrichment of methane in the natural gas attributed, by earlier workers, to be a consequence of fractionation during secondary migration (post-expulsion) has been proven to be real also during expulsion at least for pyrolysis conditions.

Appropriate use of pyrolysis method; such as pyrolysis of coarse grain samples in open system, has the potential to expel gas closer in composition to natural gas. We have shown that by using one order of magnitude higher grain size than conventional powder samples, methane content in the gaseous products of the pyrolysis increases. A special experimental set-up developed during this study has the potential to replace the conventional pyrolysis of powder samples in studies aiming at the determination of gas generation potential of, and composition of expelled gas from, a given source rock.

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References

generation and expulsion from source rocks by open and restricted system pyrolysis experimentations. Part II. Implications for natural gas composition. In the Abstract Book of the 14th International Symposium on Analytical and Applied Pyrolysis, Seville, Spain, 2–6 April 2000, p. 49.


