

EVALUATION OF FACTORS INFLUENCING THE THERMAL
MATURATION OF ORGANIC MATTER
DURING CONFINED PYROLYSIS EXPERIMENTS.

Raymond MICHELS, Patrick LANDAIS,
Marcel ELIE, Laurence GERARD and Laurence MANSUY.

CNRS-CREGU - BP 23, 54501 Vandoeuvre Cedex. FRANCE.

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INTRODUCTION

Pyrolysis of organic matter can be dedicated either to investigate its chemical structure or to mimic the transformations induced by subsidence in sedimentary basins i.e. thermal maturation. Reproducing natural geological conditions has been for a long time strictly considered as a matter of time and temperature. More recently, the roles of water, pressure, mineral content and type of autoclave have been investigated. However, few studies offered the opportunity to adjust and control these different parameters in order to evaluate their respective influence on the thermal maturation of kerogens and source-rocks. The present paper summarizes the results of confined and hydrous pyrolysis experiments dedicated to re-evaluate the validity of the technique and determine the influence of the experimental conditions.

EXPERIMENTAL

Confined Pyrolysis : 200 mg of kerogen or 1-1.5 g of source-rock are introduced in gold tubes ($\phi = 0.5$ or 1 cm; L = 5 cm) under argon atmosphere. The sealed gold tubes are placed in stainless steel autoclaves and isothermally heated at temperatures ranging between 250 and 400 °C for 72 hours under pressures ranging between 300 and 1300 bars (1). At the end of each run, gold tubes are pierced and their organic content washed and extracted with chloroform.

Hydrous Pyrolysis : about 400 mg of rock are isothermally heated for 72 hours in a stainless steel autoclave in the presence of an excess of liquid water. The rock sample is covered by pure liquid water and the headspace is filled with helium (2). The pressure inside the autoclave is due to the expansion of water and to the generation of oil and gas but rarely exceeds 330 bars. The theoretical maximum pyrolysis temperature is limited by the supercritical temperature of pure water (374 °C) and generally set to 350 °C because of the generation of CO₂ and hydrocarbons. At the end of each run, the autoclave is cooled, gases are collected, floating oil (expelled oil) recovered and rock chips collected for subsequent extraction.

High Pressure Hydrous Pyrolysis : Because in conventional hydrous pyrolysis devices, internal pressure depends on the initial filling of the autoclave (water + rock) and on the temperature, high pressure hydrous pyrolysis runs were performed in order to test the effect of increasing pressures on the hydrocarbons expulsion and generation. The use of a high pressure system (pump + autoclave) allows water to be injected inside the autoclave as soon as the isothermal stage is reached and to adjust the pressure to the desired value (300, 700 and 1300 bars in the present work). The recovery of oil and gas is similar to that described for conventional hydrous pyrolysis.

TEMPERATURE CHOICE

Most of the artificial maturation series are generated using temperature steps of 30 to 50 °C. Nevertheless, in order to describe the complete thermal evolution of an immature organic matter, it can be necessary to perform more pyrolysis runs (3). For example, the different maturation stages of a Mahakam coal were fully evidenced only when using a 10 °C pyrolysis step. The maximum generation of polar compounds, aromatics and saturates occurring at 320, 330 and 340 °C respectively. Similarly, this was the only way to define the chronology of the transformations affecting both the solid residue and the soluble fraction.

CHOICE OF THE TIME-TEMPERATURE PAIR

In order to compensate geological times, pyrolysis experiments use higher temperatures than those noticed in natural environments. Several hours to several years experimentations have been carried out and generally show that long term experiments improve the quality of the simulation. On the other hand, comparison of the analytical data derived from 5 hours to 100 days experiments on an immature Mahakam coal has evidenced the influence of time-temperature pairs on the composition of both solid residues and CHCl₃ extracts. It is shown that saturates content increases with experimentation time (4). As far as CHCl₃ extract / TOC ratios are similar for a given Time Temperature Index (Arrhenius TTI), such evolution evidences the increasing effect of secondary cracking in long term experiments. Furthermore, the expulsion of oil from source-rock is enhanced in long term experiments (Paris Basin shale).

KEROGEN vs. WHOLE ROCK

Heating experiments can be performed either on whole rock or on kerogen concentrates. While kerogen pyrolysis allows more structural parameters to be investigated and catalytic effects to be ignored, whole rock pyrolysis takes into account the transformation of all the rock components

(organic + mineral) (5, 6). However, kinetics of clay minerals transformations cannot generally be extrapolated to temperatures higher than 300 °C and organo-mineral interactions are not easily duplicated. Then, the extent of the modifications of the maturation process related to the behaviour of the mineral matrix cannot be accurately determined. Results from confined-pyrolysis experiments on the Woodford shale have shown that the peak generation of hydrocarbons as well as the onset of the petroleum potential decrease always occur earlier for kerogen than for whole rock (Figure 1).

EFFECTS OF PRESSURE

The role of pressure in the simulation of organic matter thermal maturation has not been widely investigated. However, recent results have demonstrated that the rates of hydrocarbon cracking (7) as well as the activation energy (8) were pressure dependant. It is generally accepted that increasing pressures induce a delay in oil genesis and in kerogen transformation (9). In the present work the role of pressure has been studied in both confined and hydrous pyrolysis systems.

The effects of pressure on isolated kerogen or coal transformation are minor and necessitate a careful control of temperature ($\pm 1^\circ\text{C}$) to be shown. No clear variations in the extract yield or in the Rock-Eval HI and Tmax have been noticed. However, a bimodal distribution of n-alkanes has been observed on GC traces for low pressure experiments (300 bars) on a type II kerogen. Furthermore the pristane/phytane ratios are systematically lower in high pressure experiments (1300 bars) whereas the evolutions of the Pr/nC17 and Ph/nC18 ratios are not pressure dependant. Similar results have been obtained when increasing the dead volume in gold tubes by decreasing the amount of kerogen (Mahakam coal) to be pyrolyzed from 200 mg to 50 mg. Spectroscopic studies of total extracts (^1H NMR, ^{13}C NMR, IR and synchronous UV fluorescence) also allowed pressure-dependant structural parameters to be recognized.

High pressure hydrous pyrolysis experiments on whole rock (Woodford shale) revealed that amounts of expelled oil and total yield (expelled + extracted) were highly dependant on pressure. Figure 2 confirms that high water pressure delays and hinders the genesis and expulsion of hydrocarbons. On the other hand, results from confined pyrolysis did not reveal an important control of pressure neither on the genesis nor on the expulsion of oil. The total yields maxima are similar but can be shifted of 50 °C (Figure 3) while expulsion maxima occur at the same temperature (330°C).

EFFECT OF WATER

The effect of water on the artificial maturation of organic matter is still a subject of controversy. Addition of water in confined experiments on Mahakam coals did not seem to give detectable effects (10). On the other hand, the role of water during organic compounds pyrolysis has been frequently emphasized (11).

Such situation can probably be related to the unavailability of analytical data derived from hydrous and confined pyrolysis experiments performed on the same rock and in the same P-T-t conditions. Furthermore the analytical procedures for oil and gas recovery as well as shale extraction cannot be identical for both types of pyrolysis. For example, the "expelled fractions" corresponding to floating oil and to cold chloroform washing in hydrous and confined pyrolysis respectively cannot be simply compared.

As far as pressure can be controlled, experiments conducted in a high pressure hydrous pyrolysis system can be compared to those performed in confined pyrolysis. On Figure 4 are reported the expelled/washed as well as extracted fractions obtained on hydrous and confined Woodford shale pyrolyzates at 700 bars. Despite some discrepancies concerning the maximum temperature for extract yield, a general agreement can be noticed in the trends as well as in the amounts of generated and expelled hydrocarbons. Similarly, the addition of water in gold tubes (10, 50 and 100 wt % of shale) did not significantly modify the oil expulsion rate. However, when hydrous pyrolysis experiments are carried out in low pressure conditions ($P < 200$ bars), the total oil yield is much more important than in confined and high pressure hydrous pyrolysis systems (see Figure 2, open circles).

SUMMARY

The examination of various sets of data deduced from organic matter pyrolysis in closed systems (confined and hydrous) revealed that experimental conditions must be carefully defined:

- A wide range of temperatures can be useful in order to determine the various stages of hydrocarbons generation and kerogen transformations.
- Long term experiments induce secondary cracking reactions that chiefly affect polar compounds.
- Pressure effects on oil generation and expulsion in confined pyrolysis system are not as determinative as in hydrous pyrolysis. However, variations of external pressure as well as effluents pressure can significantly modify the distribution of the generated hydrocarbons.
- In order to evaluate the role of water in organic matter maturation, hydrous and anhydrous pyrolysis must be conducted in the same experimental conditions (temperature, pressure, time).
- When performed in the same T-P-t conditions, confined and high pressure hydrous pyrolysis can generate and expell similar amonts of hydrocarbons.

These observations strongly suggest to take into account other experimental parameters than time and temperature when simulating organic matter thermal maturation. They also support further work on the comparison of the different pressurized pyrolysis systems used to reproduce the natural transformations of organic matter.

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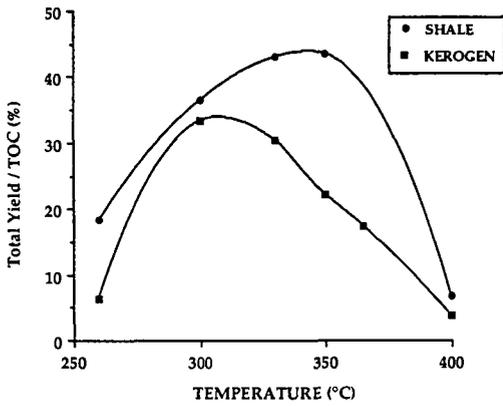


Figure 1: Comparison of the total yield evolution during the confined pyrolysis of type II shale and extracted kerogen

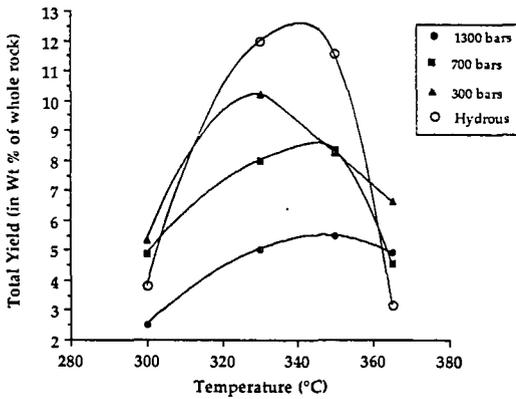


Figure 2: Effect of pressure on oil generation during hydrous and high pressure hydrous pyrolysis of a Woodford shale.

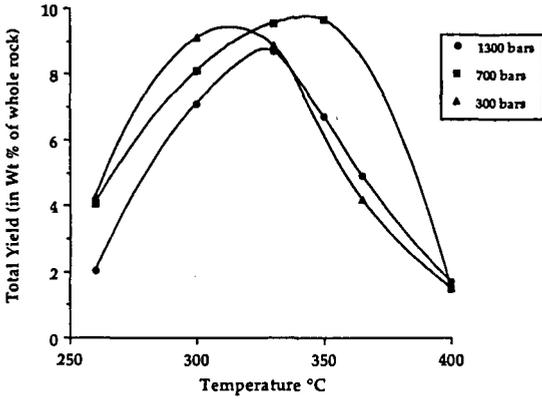


Figure 3 : Effect of pressure on the generation of hydrocarbons during the confined pyrolysis of a Woodford shale.

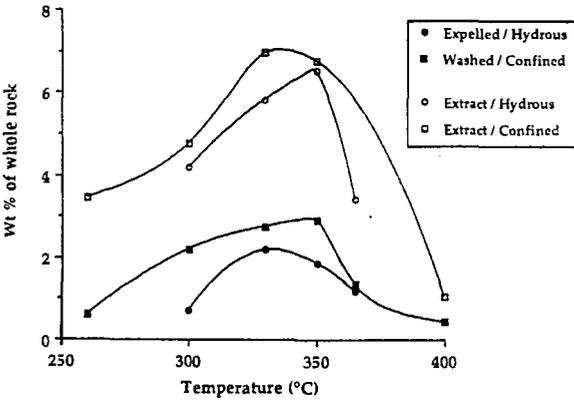


Figure 4: Comparison of the evolution of generated and expelled fractions during the high pressure hydrous and confined pyrolysis at 700 bars.