

## PROCESSES LEADING TO INCREASE OF ALKYL CHAIN LENGTHS UNDER HYDROUS PYROLYSIS CONDITIONS

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### KEYWORDS:

Hydrous pyrolysis, polymerisation, short-chain carboxylic acids

### INTRODUCTION

In the last decades, various kinds of pyrolysis procedures have been used to simulating petroleum generation from source rocks or kerogen, and the effect of water on the saturated hydrocarbon yields has been a matter of debate. Pyrolysis processes tend to give a larger proportion of both unsaturated compounds and polar compounds than in natural petroleum, where the aliphatic hydrocarbon fraction is normally the major constituent. Confined system pyrolysis with excess water present during pyrolysis results in a more hydrocarbon-rich product with a composition more similar to natural petroleum than products from unconfined and dry pyrolysis (Lewan, 1997). Confined pyrolysis in gold tubes, with a compressed gas phase and some excess water produced in the initial reactions, also give a high proportion of aliphatic products (Michels *et al.*, 1995).

The generally accepted model for hydrocarbon generation assumes that a given quantity of aliphatic chains is present in the polymeric kerogen material, and is released in the thermal cracking of the polymer. In this model, water functions as a hydrogen donor and increases the amount of saturated products after an initial cracking step. In confined systems with less water, other constituents, including hydrogen gas produced during pyrolysis, may function in a similar way. However, both models imply that the total amount of aliphatic compounds possible to generate is limited by the amount of alkyl units initially incorporated in the starting material.

However, pyrolysis experiments with simple compounds show that polymerisation type reactions producing liquid phase products also occur. Investigations on the thermal stability of organic acids in formation waters (Andresen *et al.*, *in press*) and gases in hydrothermal systems (Berndt *et al.*, 1996) show the generation of larger hydrocarbon molecules from small reactants. To explain such observations, polymerisation reactions of gaseous molecules with water involved in the reaction seem the most relevant pathway.

In this presentation, observations of alkyl chain generation in "classical" hydrous pyrolysis of simple compounds will be shown to reproduce the series of homologous organic acids found in waters in the vicinity of oil, and also contribute to the long-chain hydrocarbon compounds that are found in the petroleum phases. The possibility of a Fischer-Tropsch mechanism for the polymerisation step will be discussed.

### EXPERIMENTAL

Hydrous pyrolysis of simple organic compounds has been performed in stainless steel autoclaves. In one series of experiments, formic acid (HCOOH) is used as the organic reactant. The gaseous, aqueous and extractable products have been analysed for an experimental design on the experimental conditions, varying the parameters in the following range: *Reactors*: Parr 71 ml(=L), SS tubes 10 ml (S); *Temperatures*: 300-380 °C; *Head-space to liquid volume ratios(subcritical)*: 0.1-0.9; *Water/formic acid ratio*: 0 - 9; *Presence of mineral phase (goethite)*: present/absent; *Oil phase (cyclohexane)*: present/absent. All experiments have had a duration of 72 hours. After the experiment, quantitative analyses were made of the generated gas phase for hydrocarbon gases including hydrogen and carbon monoxide in some cases, the aqueous phase was analysed for content of dissolved organic compounds and the oil phase products were extracted, quantified gravimetrically and analysed by GC.

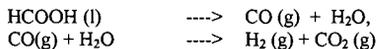
For comparison, the results from similar experiments are given for a Kimmeridge source rock.

## RESULTS AND DISCUSSION

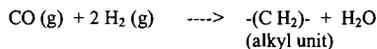
Products with increased alkyl chain length were consistently found both in the gas phase and aqueous products. In the experiments using the small reactors, wax profiles were observed in the extractable organic fraction (Figure 1). Selected experimental results are summarised in Table 1.

The results confirm observations from previous experiments with acetate cracking in gold tubes, which gave generation of a wide spectrum of longer-chain products, including C<sub>3</sub>-C<sub>6</sub> hydrocarbon gases and C<sub>7</sub>+ hydrocarbons with chain lengths up to C<sub>32</sub> (Andresen *et al.*, *in press*). Considerable levels of carbon monoxide was also found in the gas phase, while hydrogen was not analysed.

In the new experiments with formic acid (HCOOH) as the starting material, polymerisation reactions is the only possibility for generation alkyl chains. Formic acid rapidly decomposes and reacts with water upon heating:



and the products can polymerise by a surface catalysed Fischer-Tropsch mechanism:



Carboxylic acids are a well-known product from such reactions. The distribution of homologues expected from this mechanism correspond to the distribution generally observed in oil-field waters, with an exponential reduction of concentration relative to acetic acid with increasing carbon number. This distribution has also been observed in all hydrous pyrolysis experiments performed at this laboratory, and it seems to be

completely independent of the type of organic starting material (single compounds, biomass or sedimentary organic material).

As shown by the results given in Table 1, there is a considerable effect from variations in the reaction conditions with regards to the product composition. The choice of reactor is one major factor. n-Alkanes in the wax range, as shown in the chromatogram in Figure 1, were found in higher than trace amounts only in the experiments using the small stainless steel reactors. This can be caused either by differences in the catalytic activity of the reactor surfaces, or by the relatively higher loading in the small reactors, which will give higher concentrations of reactive gas phase species. At present it is not clear what is the limiting factor for the alkane formation.

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**Table 1. Composition of products from selected pyrolyses**

Reaction conditions	Gas phase (% of initial C)				Aqueous acids (mM)			HC chains ?	
	CO <sub>2</sub>	CO	CH <sub>4</sub>	H <sub>2</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>		
<b>Formic acid</b>									
S/330 /-w	Not measured				0.75	17.10	4.92	C <sub>7</sub> -C <sub>25</sub>	
S/330 /-w,+min.	Not measured				0.60	10.28	2.34	C <sub>8</sub> -C <sub>28</sub>	
S/300 /-w (Fig.1)	Not measured				3.03	3.34	0.63	C <sub>8</sub> -C <sub>31</sub>	
S/380 /-w	Not measured				0.50	3.39	1.91	C <sub>9</sub> -C <sub>32</sub>	
S/380 /+w,+C C <sub>14</sub> -C <sub>32</sub>	Not measured					3.30	7.26	1.18	
S/380 /+w,	Not measured				2.96	3.93	0.89	C <sub>19</sub> -C <sub>31</sub>	
L/330 /+w,+min.	46.5	n.m.	0.18	n.m.	0.82	0.76	0.56	-/trace	
L/380 /+w,+C /trace		43.8	n.m.	0.28	n.m.	6.28	1.21	0.10	
L/380 /+w,+min.+C	70.4	n.m.	0.07	n.m.	0.51	0.50	0.004	-/trace	
L/380 /+w	18.6	n.m.	0.02	n.m.	0.49	0.12	0.09	-/trace	
L/330 /+w	23.6	0.76	0.02	n.m.	0.98	0.09	0.05	-/trace	
L/330 /+w,+min	16.3	0.26	0.02	n.m.	0.58	0.74	0.15	-/trace	
<b>Kimmeridge source rock -standard hydrous pyrolysis (Barth et al. 1989 )</b>									
L/300 to >C <sub>29</sub>		4.8	n.m.	0.4	0.06	tr	13.15	2.45	up
L/330		7.8	n.m.	1.3	1.84	tr	14.26	2.71	
L/350 C <sub>10</sub> -C <sub>30</sub>		10.4	n.m.	1.5	1.75	tr	12.38	2.80	

n.m.: Not measured

- : Below detection level

**Figure 1.**

**Gas chromatogram of the alkane profile from experiment 3, Table 1.**

Column: HP-5, 25m; Temperature program: 40°C\*1 min, 6°C/min to 290°C \*5 min., FID detector.