

## RETARDATION OF OIL CRACKING IN HIGH-PRESSURE LIQUID WATER

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Oil cracking in geological basins is generally simulated using laboratory pyrolysis experiments in which the oil is heated in either a vapour or a mixed water-vapour phase in a closed system. However, in geological basins, oils exist in water-saturated conditions with the water being either hydrostatically pressured or over-pressured. Previous investigations into the effects of pressure, mainly in gold bags, have indicated that pressure effects are not significant. In contrast, studies under inert gas pressure have suggested the cracking is retarded. The overall aim of this investigation has been to investigate the effect that liquid water pressure has on oil cracking in geological basins. Using a stainless steel pressure vessel rated up to 500 bar (*ca.* 7000 psi, 50 MPa) at 350°C, cracking of an oil was compared under anhydrous, normal hydrous conditions, a full vessel of water at the steam pressure of 150 bar and liquid water pressures of 310 and 470 bar.

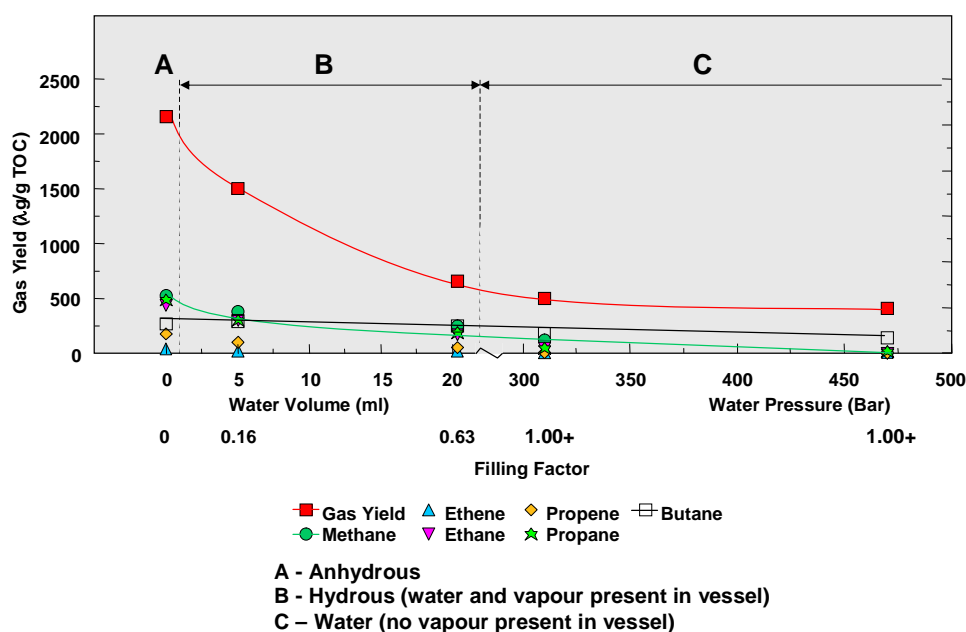


Figure 1. Total C<sub>1</sub>-C<sub>4</sub> and individual hydrocarbon gas yields from the oil cracking tests.

The principal findings are:

- (i) cracking of oil to C<sub>1</sub>-C<sub>4</sub> hydrocarbons is retarded significantly by high-pressure liquid water (Figure 1), and the magnitude of this effect is much more pronounced than in other studies using gold bags or inert gas pressure and there is evidence that pressure alters the dryness of the gas;
- (ii) increasing the water filling factor also reduced the hydrocarbon gas yield at constant steam pressure (Figure 1) but also reduced the boiling point range of the oil, indicating a major change in product selectivity; and
- (iii) In tandem with the vastly reduced hydrocarbon gas yields at high pressure, some polymerisation to increase both the boiling point range and asphaltene content of the oil was evident, consistent with volume reduction processes being favoured at high pressure.

To provide further initial insights into these phenomena identified, a corresponding set of experiments was conducted on *n*-hexadecane at 350°C where, previously, only gold bags have been used to investigate pressure effects (Jackson *et al.*, 1993. The product distribution from the anhydrous pyrolysis was entirely consistent with previous studies (Ford, 1986) with the conversion being low (*ca.* 2 %) due to the relatively low temperature of 350°C used to ensure being below the supercritical temperature of water. Overall, apart from the inherent lower conversions, the experiments revealed very similar trends as for the oil, notably the vast suppression in C<sub>1</sub>-C<sub>4</sub> hydrocarbon yields in the water pressure experiments, which was accompanied by a marked decrease in the yield of C<sub>5</sub>-C<sub>8</sub> hydrocarbons in the liquid product, together with the suppression of alkene formation at high liquid water pressures. Further, the re-arrangement of *n*-alkanes to high molecular mass (>C<sub>16</sub>) branched chain alkanes was suppressed by the combination of increasing water content in the vessel and the increasing liquid water pressure. Increasing the amount of *n*-hexadecane 4 fold at 500 bar had no significant effect on the gas yield, confirming that over-pressurisation was not occurring within the autoclave, with the water being undersaturated with respect to hydrocarbon gas at 350°C. These results provide further evidence that oils cannot crack to a significant extent under the water pressure regimes found in geological basins.

## REFERENCES

- Ford, T.J. 1986. Liquid-phase thermal decomposition of hexadecane: reaction mechanisms. *Ind. & Eng. Chem. Fund.* 25, 240-243.
- Jackson, K.J., Burnham, A.K., Braun, R.L. and Knauss, K.G. 1995. Temperature and pressure dependence of *n*-hexadecane cracking. *Organic Geochemistry* 23, 941-953.