A novel hydropyrolysis approach for optimum release of covalently-bound biomarker hydrocarbon skeletons from sedimentary organic matter

G. D. Love
I. P. Murray
C. E. Snape

Fuel Research Group, University of Strathclyde, Dept. of Pure and Applied Chemistry, Thomas Graham Building, 295 Cathedral St., Glasgow G1 1XL, UK

In order to generate more representative biomarker profiles, geomacromolecules must first be fragmented into smaller (readily-analysable) structural units to gain access to the covalently-bound pool of biomarkers. Existing chemical degradation and pyrolysis methods for fragmenting and analysing molecular components of kerogen are notoriously poor at providing quantitatively significant and/or accurate data. Chemical degradation methods have been less successfully and less widely applied to kerogen in comparison with solvent-soluble macromolecular fractions (usually applied to *polar* fractions). In general, since the polar fractions represent only a small proportion of the total OM and the yields of routinely analysable products obtained from chemolysis are low, it follows that the biomarker profiles produced from chemical degradation may also be highly biased with respect to the total biomarker assemblage. With analytical pyrolysis methods, e.g. Py-GC-MS, higher conversions of kerogen can be achieved but the structural information about the molecular constituents that is provided (and hence the accuracy of biogeochemical information that is conveyed) is compromised to a significant extent due to the appreciable secondary reactions (cracking and isomerisation) of released products which manifest at the high pyrolysis temperatures employed (typically >600°C). In order to generate more representative biomarker profiles, a far higher proportion of the biomarker constituents must be accessed. Reaction conditions are sought which solubilise a significant proportion of sedimentary OM (approaching 100% conversion), whilst maximising the level of structural (biogeochemical) information and minimising the extent of secondary reactions between degradation products.

Pyrolysis at high hydrogen pressures (> 10 MPa, *hydropyrolysis*) eliminates the problem of low yields often associated with the use of sterically-bulky chemical reagents and limits the extent of retrogressive chemistry (leading to char-formation and rearrangement of detectable products) encountered in other analytical pyrolysis methods (e.g. flash-pyrolysis). Fixed-bed hydroyrolysis in the presence of a dispersed sulphided molybdenum catalyst gives rise to overall carbon conversions greater than 85% for petroleum source rocks (Type I and Type II ancient SOM) and high volatile coals (Type III OM), with high selectivities to dichloromethane-soluble tar and low hydrocarbon yields (Roberts *et al.*, 1995). Previous work has demonstrated the unique ability of fixed-bed catalytic hydropyrolysis to release much higher yields of aliphatic biomarker hydrocarbons (including *n*-hydrocarbons, hopanes, steranes and methyl steranes) from immature kerogens in comparison with solvent extraction, mild catalytic hydrogenation and normal pyrolysis methods (Love *et al.*, 1995, 1996). A combination of slow heating rate (5°C min^{-1}), high hydrogen pressure (15 MPa) and use of a dispersed sulphided molybdenum catalyst represents the best regime for achieving high conversions to dichloromethane-soluble products whilst minimising the structural rearrangement of biomarker species (Love *et al.*, 1997). Staged hydropyrolysis on Goynuk oil shale (NW Turkey, Oligocene, Type I) has confirmed that hopanes released at higher temperatures (above 350°C) through cleaving relatively strong bonds (possibly by up to 4 or more ether linkages protected by a macromolecular matrix) are quantitatively more significant than those released at lower temperatures for this immature source rock with a relatively low organic sulphur content (Love *et al.*, 1997). This important pool of (strongly-)bound biomarkers is especially difficult to isolate by existing chemical and thermal degradation methods. The very high yields of products, in combination with the retention of structural information that is observed, dictates that hydropyrolysis will generate a more sensitive and accurate biomarker profile for sedimentary OM than these existing approaches.

Novel two-stage hydropyrolysis system

A new version of the hydropyrolysis technique has now been devised which results in improved release of biomarker hydrocarbons from sedimentary OM. This new experimental set-up incorporates additional *in-situ* catalytic defunctionalisation of primary vapours produced from initial hydropyrolysis. This results in a significant decrease in the heteroatom content and average molecular weight of the collected pyrolysate (through, principally, reductions in S,O and N contents), resulting in a concomitant increase in the amount of hydrocarbon products without promoting significant additional structural rearrangement of the biomarker carbon skeletons. This is of great importance since constituents of non-hydrocarbon fractions are, largely, too polar and/or non-volatile to be readily analysable by routine chromatographic techniques. Furthermore, the high-molecular-weight species produced from single-stage hydropyrolysis (and, indeed, from all degradation regimes) are likely to contain appreciable amounts of important sequestered biomarker species. Thus, the use of two-stage hydropyrolysis for geomacromolecule degradation increases the amount of biogeochemical information available to the geochemist.

Figure 1 shows a schematic representation of the two-stage hydropyrolysis apparatus. In the upper zone of the reactor, catalytic hydropyrolysis of SOM (typically 50-500 mg) is performed by resistive heating from ambient temperature to 100°C at 50°C min^{-1} then to 500°C at 5°C min^{-1} using a hydrogen pressure of 15.0 MPa as described previously (Love *et al.*, 1995, 1996). A continuous hydrogen flow of 10dm^3 min^{-1}, measured at ambient temperature and pressure, through the reactor ensures that the overall is not limited by mass transfer in the sample bed and so, once formed, the volatiles quickly escape. The primary vapours produced from hydropyrolysis are then swept over a bed of hydrotreating catalyst (c. 1 g of γ-alumina-supported Ni/Mo catalyst) which is positioned in the lower zone of the reactor tube. This lower zone is held isothermally at 300°C throughout the entire pyrolysis process to achieve effective (reductive) removal of select heteroatom functionalities (including ether, sulphide, carboxyl, hydroxyl, thiols and thiophenic groups) while minimising the extent of thermal cracking and rearrangement of carbon skeletons of released organic products. The pyrolysate is collected in a dry ice-cooled trap and recovered in dichloromethane for subsequent product fractionation.

This new system is also capable of selective defunctionalisation of the polar or asphaltene phase of source rock extracts or petroleum, which have been shown to contain appreciable amounts of incorporated biomarker structures (e.g. Hoffmann *et al.*, 1992). In these cases, the samples are pre-loaded on a suitable adsorbent, such as alumina, to prevent them from softening and escaping from the reactor prior to pyrolysis/volatilisation.

The net effect of this new system is to release biomarker skeletons in a more readily analysable form for GC and GC-MS. In particular:

i) a more accurate estimate of the total pool of covalently-bound biomarkers (in polar, asphaltenes and kerogen samples) can now be obtained for the first time, and

ii) the relative abundance of specific biomarker constituents, with respect to the total biomarker assemblage, may be more accurately assessed.

Therefore, the use of two-stage hydropyrolysis provides more representative biomarker profiles for SOM than can be achieved by existing methods.

Results

Model compounds have been used to assess the selectivity of the hydrotreating stage. From the results obtained thus far, it apparent that by maintaining the hydrotreating catalyst bed at 300-320°C, then defunctionalisation of certain heteroatomic functional groups (including alcohol, ether, sulphide and carboxylic acid) occurs without causing significant cracking of the carbon skeletons of organic compounds. For example, almost complete reductive conversion (>90%) of octadecan-1-ol (approximately 100mg) to, principally, octadecane (plus smaller amounts of octadec-1-ene) is achieved in the two-stage hydropyrolysis apparatus. The reactivity of other functional groups (including olefins and aromatic rings) is presently being investigated.

From the limited number of (pre-extracted) Recent and ancient sediments subjected to two-stage catalytic hydropyrolysis, the total yields of aliphatic products are typically double those obtained by single-stage hydropyrolysis. As anticipated though, yields of different biomarker compounds increase by varying factors. The geochemical implications of the changes in the relative amounts of biomarker compounds which occurs with increasing product yield will be discussed.

Elemental analysis of the spent hydrotreating catalyst, following two-stage hydropyrolysis of sedimentary OM samples and model compounds, indicates that only trace amounts of carbon are present. This indicates that deposition (and hence, loss) of organic species, in particular, heavy tar components, on the catalyst bed is not significant at the temperatures used (300-320°C) in the lower reactor zone.