Recent developments in the calorimetric and thermoanalytical approaches to problems related to fossil fuels (genesis, extraction and use)

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Abstract – The specific interest of calorimetry and thermal analysis in the complex field of fossil fuels is illustrated here on one hand for the thermal degradation of kerogens (where the possibilities of Controlled reaction Rate Thermal Analysis are examined in its association with mass spectrometry) and on the other hand for the adsorption of surfactants or polymers in the scope of Enhanced Oil Recovery (where the possibilities opened these last years by immersion, batch and liquid flow microcalorimetry are successively examined and compared).

INTRODUCTION

Fossil fuels are fascinating for a number of reasons : of course for their tremendous *economical interest* (still to be improved), but also for the *difficulty to find* them *or to recover* them with a high yield, for their *complexity*, for their *long* and partly unknown *history*, and for the terribly *small yield of the natural process* since less than 0.1% of the oil eventually produced was able to find a satisfactory geological reservoir to wait quietly for its discovery by men ... (Ref. 1).

The complexity of these fossil fuels leads to draw the best from the simultaneous use of a large number of physico-chemical methods. One possibility is to make, among the latter, a distinction between those giving an information on the *macroscopic behaviour* of these materials (here we are mainly in the field of *phenomenological thermodynamics* and of *kinetics*) and those giving an information on their *molecular properties* (and which mainly includes the large variety of *spectroscopic methods*).

We are ouselves primarily interested in the *thermodynamic* and *kinetic* approaches and we shall focus our attention on 2 problems concerning fossil fuels, namely (i) the thermal *degradation of kerogens*, (ii) *adsorption* problems in the scope of *enhanced oil recovery*.

THE THERMAL DEGRADATION OF KEROGENS

The "kerogens" are defined as the insoluble part (in common organic solvents) of the sedimentary organic matter (Ref. 2). Their thermal degradation is of interest, both as *a natural geothermal phenomenon* leading to more concentrated and more valuable fossil fuels and as *an artificial transformation* similar to that of asphaltenes (very similar, in structure, to kerogens) which could be of practical interest in a different economical context.

Kerogens are highly complex and even heterogeneous since they result from the partial degradation of numerous biological materials such as plancton, algae, bacterias, pollen, superior vegetables etc..., some of which may still be detected by optical microscopic observation. It is therefore not surprising to learn that a large number of chemical functions and elements (including C, H, O, S, N, V ...) are found in this material. The unknown steps taking place during the thermal degradation of kerogens are much too numerous to lend themselves to a *thermodynamic* study based upon the determination of *overall changes* (of enthalpy, mass, composition etc ...) between two equilibrium states. On the other hand, a *kinetic* approach, although usually much less accurate than the thermodynamic one, may be expected to be (provided some specific conditions are fulfilled, as we shall see later) much more efficient for separating simultaneous reactions having different kinetical responses to the same environmental stresses. In other words, we expect the kinetic study to be a more efficient "lancet" of this complex degradation than the thermodynamic approach.

Nevertheless a few problems make that most thermoanalytical methods are not suitable for such a kinetic study. Some problems are common to any thermal decomposition and are usually known as the "effect of sample size", the "effect of gas flow rate", the "effect of crucible size and shape" or still the "effect of heating rate". Actually, although this is most often overlooked, *the above effects are only secondary effects of the lack of uniformity*, within the sample, of the environmental stresses (usually essentially the temperature and the atmosphere composition) producing the thermal transformation under study. One other problem is now specific to complex thermal decompositions (we are calling here "complex" a

thermolysis giving rise to *several gaseous products* which may evolve either simultaneously or successively, with possible overlapping). The problem is the difficulty, at any time, to define *one* extent of reaction ξ_i from a single determination of the mass lost (in a TG experiment) or of the heat exchanged (in a calorimetric or DTA experiment), since several unknown reactions (leading to *several "extents of reactions"*) may take place simultaneously.

A thermoanalytical method suited for the above type of study will then have, as much as possible, (i) to ensure a uniform distribution of stresses within the sample and (ii) to follow only *one* reaction at a time. Both conditions are fulfilled by an *interacting association of Controlled reaction Rate Thermal Analysis* (CRTA)(Ref. 3) *with Evolved Gas Analysis* (EGA). Here, EGA is carried out using a quadrupole mass analyser and a turbomolecular pump. Nevertheless, this conventional method is fundamentally changed (in order to enter the scope of CRTA) in the following way (cf. Fig. 1) : the mass signal corresponding to *one selected species* (and therefore to a partial pressure P_c), is continuously fed to the heating control of the furnace surrounding the sample. In these conditions, the sample is automatically heated so that *the partial pressure P_c and the rate of production* of the selected species *are kept constant* throughout the thermal degradation (Ref. 4). It follows that the temperature and pressure gradients within the sample may be lowered at will. Moreover, provided the selected (and controlled) species is produced by one isolated reaction at a time, then the extent of reaction ξ_i may be correctly determined at any time for that reaction. Finally, the recording of temperature *vs* time (i.e. *vs* the amount of that peculiar species evolved) may be called a *"partial TG curve"*. It is indeed a *TG curve* because it gives a mass loss
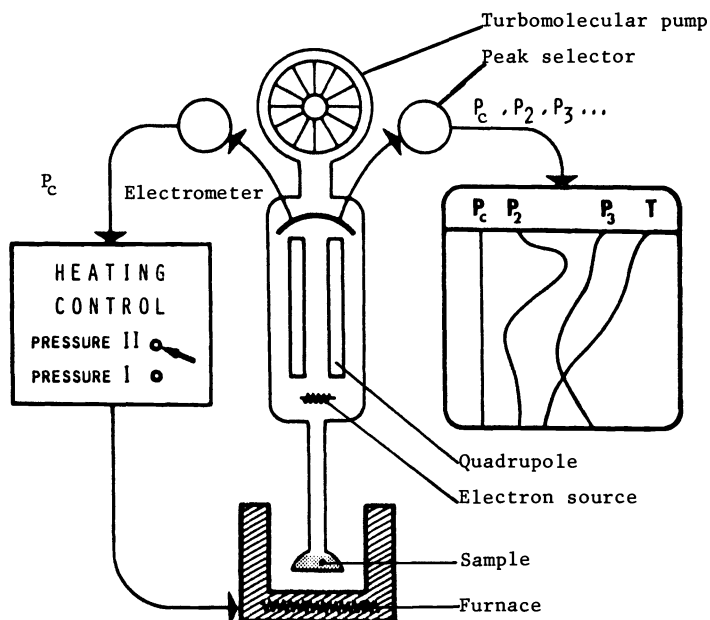

Fig. 1. Principle of Controlled reaction Rate Thermal Analysis
(CRTA) with Evolved Gas Analysis (EGA).

(as measured by the mass spectrometer, an excellent instrument, in principle, to carry out TG experiments, as noticed earlier by J. Dollimore et al. (Ref. 5))*vs* temperature. It is a *partial* TG curve because it is similar to that obtained by a hypothetical thermobalance which would detect the mass changes occuring from the evolution of one selected species only. Applying the *rate-jump method* for determining the activation energies (Ref. 6)(here, the rate of reaction periodically swings between 2 values obtained by appropriate setting of the heating control at pressures I and II (cf. Fig. 1) and leads to the gas-flow and temperature recordings represented in Fig. 2) allows to follow accurately *the* isolated reaction studied.

Typical "partial TG curves" for 3 kerogens are reported in Fig. 3. The kerogens were selected from the same evolution path (type III, following the classification, widely used to-day, of Tissot et al. (Ref. 7)) but at increasing depths of burial and therefore at increasing rates of degradation in the order A, B, C. For these recordings it is the partial pressure of H_2O which was kept constant (dashed line) and, therefore, the TG curves (solids lines) are giving the partial mass loss of H_2O exclusively (the scale on the right is given in hours but may easily be converted into mass, knowing that, in these experiments, the mass loss is
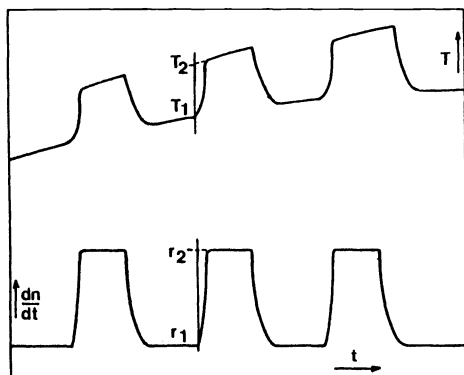
Fig. 2. Partial gas-flow recording (bottom) and corresponding
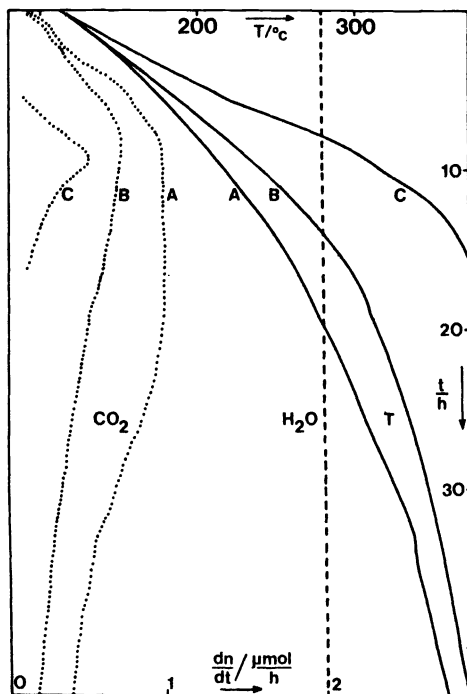temperature recording (above) for the *rate-jump method*.

Fig. 3. "Partial TG curves" (the 3 solid curves, as obtained by CRTA)
with respect to H_2O evolution, for 3 kerogens. Dashed line : check
of the constant rate of evolution of H_2O. Dotted curves : partial
dynamic pressure of CO_2 in the products of the thermolysis.

of 0.036 mg of H_2O per hour). The partial pressure of CO_2 in the gas evolved is also conti-
nuously recorded (dotted curves). These curves lead to the 2 following observations (Ref. 4):

- during the *natural* degradation (samples A to C) the CO_2-generating functions (principally
  acidic, ketonic, and the ester functions) are lost more easily than those able to generate
  H_2O
- during the *artificial* degradation of the youngest sample (A), H_2O and CO_2 are generated

with a constant ratio of 2 during nearly 1/3 of the reaction, which suggests that then they are possibly produced by the same family of reactions. This ratio of 2 is much higher than that of 0.3 which may be calculated, from the compositions, obtained by elementary analysis, for the natural transformation of sample A into sample B. This extremely large difference between a "very slow" artificial transformation and the natural one may find an explanation (i) in the *difference in pressure* : under 10^{-5} torr the gases are quickly removed, favouring unimolecular processes instead of bimolecular ones like the free-radical mechanism widely accepted to-day under higher pressures for the pyrolysis of heavy paraffins (Ref. 8) and leading to a relatively easy scission of the carbon-carbon bond ; (ii) in the *difference in temperature* : at the higher rates and therefore higher temperatures of the laboratory experiment, it seems that hydrogen elimination is favoured with respect to the C-C scission (Ref. 8) ; (iii) in the possible, although usually overlooked (Ref. 9), part played by the *surrounding minerals* during the natural transformation (our samples had been concentrated, as usually done in this type of study).

The second type of experimental determination is that of activation energies throughout the thermal decomposition (by the "rate-jump" method). For kerogen A, for instance, the activation energy for the production of CO_2 increases steadily from 120 (140°C) to 270 kJ.mol^{-1} (at 370°C). It happens that the latter value is the highest limit of the range usually reported for the thermal cracking of heavy normal paraffins (Ref. 10). It is therefore likely that the thermal cracking of kerogens in the temperature range mentioned is likely to be mainly a side-chain cracking, beginning by the weakest branched chains with various functions and ending by the strongest normal paraffinic chains.

ADSORPTION PROBLEMS IN THE SCOPE OF ENHANCED OIL RECOVERY (EOR)

General considerations

Retention of expensive chemicals (surfactants, polymers) by the rocks of the oil fields is known to be a major problem of the chemical flooding processes. A large part of this retention is due to *adsorption*, so that a good understanding of the adsorption and desorption phenomena (in the conditions of the oil field) is needed to improve the yield of the process. The general goal of this type of study is the prediction of *competitive adsorption equilibria* from brine solutions of surfactant, co-surfactant, polymer, "sacrificial" chemical and oil. This is therefore typically a *thermodynamical problem*. The number of parameters is here very large (each of the components above mentioned may actually be taken from a very large family and the adsorbents, i.e. the rocks, are themselves of various main types) but, instead of what happens with kerogens, the systems under study may be modified at will by the experimenter, so that the overall change of one state function may be related to the controlled change of one parameter. Of course, the matrix of all the experiments needed is very large but one may hope to be able to draw some general rules before the matrix is completed. From a practical point of view, the state functions needed are, for each component, the *amount adsorbed* and also the adsorption *Gibbs free energy* which is necessary to predict the displacement of one molecule by the other. In the expression of the adsorption Gibbs free energy, the *entropic* term cannot be readily assessed, whereas it was hoped, a few years ago, to reach experimentally, in a large variety of conditions, the *enthalpic term*. As we shall see, this is in good development now, whereas the entropic term has still to be estimated in various ways.

Usually, the *amounts adsorbed* must first be determined, whatever the subsequent measurements (for instance, calorimetric). It is widely accepted and extremely convenient to express the amounts adsorbed within the Gibbs model, i.e. in terms of *surface excess*. Since the latter is known to depend on the location of the hypothetical Gibbs Dividing Surface ("GDS") it is therefore highly recommended to use *reduced* surface excesses (i.e. with the GDS located in such a way that the sum of the surface excesses measured for all the components of the solution amounts to zero) or, as a second choice, *relative* surface excesses (i.e. relative to one given component which must be specified and for which the position of the GDS has been chosen so that the measured surface excess of this component is zero). Both surface excesses are correctly defined for any system. They may be given per mass unit of the adsorbent (they are then "specific") or per unit area (they are then "areal"). A clear and rigorous document prepared by D. H. Everett on these matters (including also a presentation of the experimental methods and guidelines concerning the interpretation of the adsorption data) will be shortly available from the Commission of Colloid and Surface Chemistry of IUPAC (Ref. 11). Nevertheless, since we shall be mostly interested by the calorimetric approach of the adsorption phenomena it is worth pointing out that it is often a good policy to *select a similar operating mode for the determination of the adsorption isotherms and for the calorimetric determination* of the corresponding adsorption enthalpies. This is especially true when adsorbing commercial surfactants or polymers which, even in their purest form, are most often polydisperse in chain length. In this case, the composition of the adsorbed layer (with respect to chain length but also with respect to the total amount of solute adsorbed) depends on the ratio *total amount of solute in the system / total adsorbent surface area* and not only on the apparent equilibrium concentration in the solution (i.e. without taking into account the polydispersity). This is due to a kind of chromatographic effect, with displacement of the lightest molecules by the heaviest, as well shown in the case of polymers (Ref. 12). Of course, the detection and measurement of this effect ought to be part of our knowledge on any

adsorption system involving polydisperse adsorbed molecules. Nevertheless, in the absence of convenient analytical methods for this purpose, it is essential to compare the same states (even if their definition involves specific experimental conditions) in the calorimetric experiments and in those used to determine the amounts adsorbed. In these conditions, the heat effects measured can be safely related to the excess amounts measured in the other experiment. In other words, it would not be wise, for these systems, for instance to determine the adsorption isotherm by the circulation method (otherwise excellent (Ref. 13)) if the calorimetric experiment is to be carried out with the "batch" method.

The microcalorimetric methods used

Depending on the microcalorimeter and also on the behaviour of the adsorbent in presence of the solvent one may use, in principle, either the *immersion*, or the *batch*, or the *liquid flow* method. (Speaking simply of a flow method would not allow, in the case of a calorimetric experiment, to decide whether the word "flow" refers to a heat flow or to a liquid flow).

The *immersion method*, in which the dry solid is immersed into the solution, was used several times in the past for the calorimetric study of adsorption from solutions. Nevertheless, this approach is usually not satisfactory. If the bulb containing the dry sample is completely broken (Ref. 14), then the final equilibrium is well defined but the calorimetric reproducibility is not enough for the systems studied in EOR. If only the tip of the bulb is broken, then the calorimetric experiment may be accurate but the final equilibration of the system is erratically impeded by the slow migration of the solute through the tip. Finally, if the dry sample is not initially kept in a glass bulb but in a type of container able to be widely open at the start of the experiment, then the initial state of the adsorbent may lack reproducibility (partly because of limitations in the outgassing conditions and partly because of tightness problems).

The *batch method* is more appropriate. In this method, a given amount of solution is brought in contact with a suspension of the adsorbent in the solvent, so that the techniques used may be close to those developed for reaction calorimetry (reaction of one liquid with another one). Here again, a glass bulb (containing for instance the solution) may be broken in the suspension of adsorbent, as was done by Killmann et al. to study the adsorption of polymers on silica (Ref. 15), but partly because of the limited sensitivity of the device (the bulb needs to be widely broken) and partly also because of the use of an isoperibol calorimeter (i.e. designed to follow quick phenomena like most liquid-liquid reactions) this system is not appropriate to follow the slow phenomena (i.e. lasting more than one hour) which may take place, as we shall see, during the adsorption of large molecules like those of surfactants or of polymers. A second way to operate is to mix the contents of two reservoirs (one with the suspension, the other with the solution) which are both enclosed in the measuring cell of the calorimeter. The experiment may be started either by revolving the whole calorimeter (Ref. 16,17) or by letting the solution fall from the upper reservoir down to the suspension, like from a pipette (Ref. 18). The interest of this latter way is that it may be used with commercially available equipment and that there is no problem of temperature difference between the "reactants" since they are both, from the beginning, in the same cell of the calorimeter. The main limitation is that *only one heat effect* can be measured in each new experiment (which requires a new sample and a new thermal equilibration). This is the reason for a third operating mode, in which the mother solution is introduced in a number of successive steps, from an external reservoir and through an efficient heat exchanger, with the help of a pump or a motor-operated syringe (Ref. 19,20). This procedure of course needs larger calorimetric cells than the previous ones. It was only used with the 100 cm³ cells of the standard wide-bore Tian-Calvet microcalorimeters. It saves time, adsorbent and solution. About 10 steps (and therefore 10 successive heat determinations) are usually easy to get. This is the procedure to be recommended in particular when the adsorbent does not lend itself to the liquid flow method, especially when the powder (or at least part of it) is too fine to remain on a filter or to be passed through easily by a liquid (case of pyrogenic oxides which are interesting model oxides because of their purity, large external surface area (no micro- or mesoporosity) and commercial availability, and case of clays which form another large class of adsorbents, of special interest for EOR). Recent improvements make that this technique may even be used, now, with coarse powders. The delicate problem of stirring (which must be efficient in keeping the powder in suspension but which must evolve the smallest possible thermal power, not to disturb the microcalorimetric measurement) is presently solved, in our laboratory, in the following way (Ref. 21) : we take advantage of the magnetic transmission previously suggested (Ref. 19) in order to filter the vibrations from the motor and we substantially improve the *stirring efficiency / thermal power evolved* ratio by limiting the basic motion of the propellers to a very fast half-turn followed by a (*c.a.* 10 times) slower return to the starting position. This is surprisingly easily obtained by impeding the lower magnet from rotating more than one turn. In these conditions, the lower magnet (and therefore the propellers) (i) follows the slow rotation of the upper magnet (ii) stops during slightly more than 1/2 turn of the upper magnet (iii) turns back, extremely rapidly, slightly less than 1/2 turn in order to be again parallel with the upper magnet and (iv) comes back to movement (i). The assembly is represented in Fig. 4. It is of rather universal character, may be used at temperatures up to 200°C and allows to follow adsorption phenomena (for instance slow structuring of the adsorbed layer) over hours.
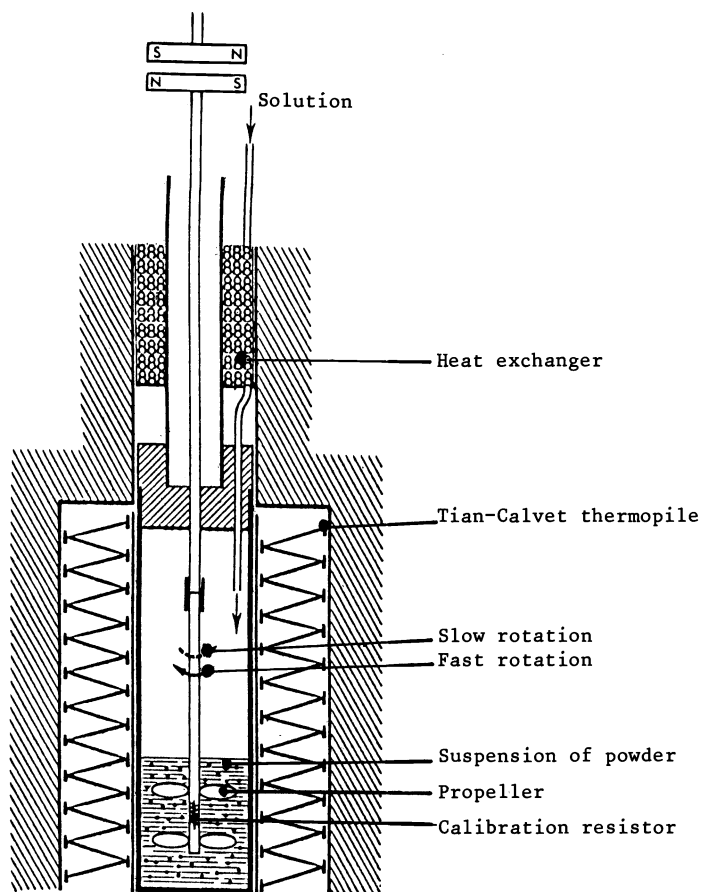
Fig. 4. Liquid adsorption microcalorimetry : batch system with
slow-fast rotation of magnet-driven propellers.

The *liquid-flow method* is less universal (since it does not accept fine powders or clays as
adsorbents) but it has its own interesting features. It allows indeed (i) to reach higher
concentrations (in the case of limited solubility of the solute) than the batch method (where
some dilution always take place) (ii) to study desorption phenomena (iii) to determine
"on-line" the amount adsorbed or desorbed by connecting an analytical device (refractometer,
UV spectrometer) to the exit port of the calorimeter (Ref. 22,23). The microcalorimeters
used are either commercially available (Ref. 24,25) or specially built for this purpose
(Ref. 23), the latter, represented in Fig. 5, being able to accomodate larger samples (in
order to increase the number of adsorption steps and therefore the resolution of the study)
but also smaller total surface areas (2.7 m² in the example given in (Ref. 23)) than the
multi-purpose commercial equipment. These microcalorimeters may be considered as the
successors of Groszek's apparatus (Ref. 26) whose simplicity does not alter the sensitivity
and resolution but brings limitations to the quantitative character of the measurement.

Concerning the thermodynamic presentation of the data, it is worthwhile noticing that

- all the calorimetric experiments reported above (with the exception of the immersion
  experiments which, as we saw, are not exactly adapted for the study of adsorption from
  solutions) involve the *displacement*, from the surface of the solid, *of solvent molecules
  by molecules of solute.*
- the heats measured are "experimental heats", depending both on the system studied and on
  the experimental procedure and they can't be called, in the absence of any clearly
  mentioned correction,"*enthalpies* of displacement" and even less "enthalpies of *adsorption*"
  (cf. above), although this is sometimes done.
- the calculation of the *enthalpy of displacement* $\Delta_{dpl}H$ (where "dpl" stands for "displacement",
  which leaves the subscript "dis" for "dissociation" only) from the experimental heat Q_{exp}
  always needs (i) to know the *amount adsorbed* and (ii) to take into account the *dilution
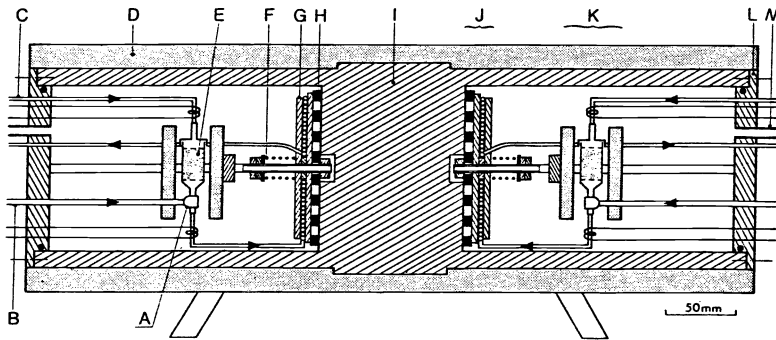 enthalpy* of the solute in the conditions of the experiment

Fig. 5. Liquid adsorption microcalorimetry : twin liquid-flow
system (K : sample cell – J : heat flowmeter – A : mixing
device for determining enthalpies of dilution).

- the path to follow for a *rigorous derivation* of the enthalpy of displacement from calori-
  metric measurements was analysed either for the liquid flow method (Ref. 23,24,27) or for
  the batch method (Ref. 20)
- as a rule, the *enthalpy of adsorption* proper cannot be usually reached, because of our lack
  of knowledge about the exact number of solvent molecules displaced by one molecule of
  solute and therefore about the corresponding enthalpy of desorption, which is included in
  the enthalpy of displacement derived from the calorimetric data. An advantage of speaking
  of an "enthalpy of *displacement* " is not only that it unambiguously corresponds to the
  phenomenon actually taking place but also that it naturally leads to indicate what species
  is displaced by which other, so that the limited (although useful) meaning of the experi-
  ment is not forgotten
- of course, it is always necessary to specify whether the enthalpy of displacement is
  differential (or partial) or *integral* and also (but this is not critical for the dilute
  solutions which are usual in EOR), when given per mole adsorbed, whether it is a *relative*
  or (more frequently) a *reduced* surface excess quantity.

Results obtained or expected in the scope of EOR
The results are still scarce, because this field is in development and because, as we saw in
the above paragraph, a number of practical and conceptual problems needed several years to
be solved. The main systems examined may be classified in the following way :

- *Surfactants* adsorbed from water solutions onto silica gel.
  Although only 5 years old to-day, the figures published by Noll et al. in 1979 on the
  "heats of adsorption" of sodium dodecylbenzene sulfonate and sodium dodecylsulfate on a
  Davison D-62 silica gel (of 340 m^2g^{-1}) are among the first in the field (Ref. 28).
  Nevertheless, they are not easy to compare with subsequent work because, in these "early
  times" the amounts adsorbed were not known for these systems.
  More recently, Denoyel et al. (Ref. 23) presented results on the adsorption of a non-ionic
  surfactant (octylphenolpolyoxyethylene, commercially available under the trade name Triton
  TX-100) on a silica gel (Spherosil of 14 m^2g^{-1}). The main conclusions are that (i) at low
  coverage the main interaction is between the adsorbate and the adsorbent (exothermal effect)
  (ii) at higher coverages the "lateral" interactions are predominant (endothermal effect)
  and give rise to a cooperative adsorption and (iii) in the case of adsorption from a
  solution close to the CMC there is a thermal compensation of both phenomena, so that the
  whole adsorption phenomenon is nearly athermal.
- *Surfactants* adsorbed from water solutions onto sand, sandstone or kaolin.
  These adsorbents are of course more realistic than amorphous silica gel, but not as easy
  to handle and study, either because of problems of sensitivity of the calorimeter (ground
  sand and sandstone have surface areas in the range of 0.05 to 4 m^2g^{-1} at most) or because
  of problems of composition (sandstone may contain small amounts of clay which often
  represent more than 90% of the surface) or because of their mechanical properties (kaolin
  cannot be studied in a liquid-flow calorimeter).
  The calorimetric study of adsorption on sandstone is still at a start (Ref. 28). On the
  other hand, the adsorption of sodium dodecylbenzene sulfonate and of several non-ionics
  "Tritons" of various length was followed calorimetrically onto ground sand and onto kaolin
  by the batch method (Ref. 18). The main conclusions are here that (i) the integral enthalpy
  of displacement (up to the plateau of the adsorption isotherm) is as low as 5 to 17 $mJ.m^{-2}$
  for the 5 systems studied and (ii) the time constant of the heat effect may be either
  similar (cf. TX-100 on ground sand) or much longer (cf. TX-100 on Kaolin) than the time
  constant of the adsorption proper, showing a slow re-structuration of the adsorbed layer
  which is therefore easily followed by batch adsorption microcalorimetry.
- *Polymers* adsorbed from water solutions onto silica gel.
  Cohen-Stuart et al. (Ref. 17) studied (by batch calorimetry) the adsorption of poly (vinyl
  pyrrolidone) onto a pyrogenic silica gel (Cab-O-Sil M-5, virtually identical to Aerosil 200).
  Their aim was mainly to check whether this technique, previously used by Killman and Winter
  for the same purpose (Ref. 29), was safe to determine the "bound fraction" of polymer on

the surface, i.e. the fraction of the adsorbed molecules which is in the form of "trains" attached to the surface and which must be distinguished from the "loops" and from the "tails" protruding into the solution. The conclusion is that, for relatively light polymers (here, M ≃ 4000) the method is as safe as NMR or EPR, whereas, surprisingly, IR spectroscopy is not suitable at all. At low coverage, the bound fraction of the adsorbed polymer molecules is close to 1 and it falls gradually to less than 0.5 as saturation is approached. The reservation concerning heavy polymers is explained by the slower kinetics of adsorption which does not allow to measure the whole thermal phenomenon with the equipment used. We think that the use of another type of microcalorimeter such as the one used in Ref. 18 , which allowed to follow an adsorption phenomenon over 8 hours, could solve this problem.

The more recent work of Killman et al. (Ref. 15) concerns the adsorption of 9 different polymers onto Aerosil 200 (then, practically same adsorbent as above) but from CCl_4 or $CHCl_3$ solutions, which are not relevant to EOR. Nevertheless, they confirm the suitability of calorimetry to determine the fraction of bound polymer.
- *Cosurfactants* adsorbed from toluene by silica gel.
  Noll et al. (Ref. 30) recently studied calorimetrically the adsorption of a series of normal alcohols (3, 4, 5, 8 and 10 carbons) on the same Davison D-62 silica gel as previously. They conclude that adsorption of alcohol from the hydrocarbon phase is a physical process (because of an enthalpy of displacement ranging from 22 to only 29 kJ.mol^{-1} of alcohol), with low maximum coverage of the surface (the molecular "parking" area increases, with the chain length, from 0.42 to 1.10 nm^2, which suggests an adsorption parallel to the surface).

CONCLUSIONS

We wish to point out the following conclusions about the on-going work in the fields examined:

a) About the *thermal degradation of kerogens* (and also coals or asphaltenes)
- The complexity of the phenomena leads to select a *kinetical approach*, most appropriate to give the maximum information about the numerous steps.
- An interacting association of Controlled reaction Rate Thermal Analysis (CRTA) with Evolved Gas Analysis (EGA) gives a powerful tool to study this or any other type of complex thermal degradation.
- This technique opens the field of "*partial thermogravimetry*", i.e. relative to *one selected species* produced by the thermolysis
- Even parallel (or overlapping) reactions can then be separated.

b) About *adsorption phenomena in the scope of EOR*
- The calorimetric methods and the corresponding processing of the data have just been developed during the last 5 years. They are now operational.
- The *enthalpies of displacement* are always very *small* (for the systems examined, usually smaller than 50 mJ.m^{-2}).
- Microcalorimetry proves to be an efficient tool to follow the *slow re-structuration* of a just adsorbed layer.
- It also proves to be suitable for determining the *bound fraction*, in the adsorbed phase, of relatively light *polymer molecules*. We anticipate that satisfactory results could also be obtained for heaviest polymers, provided the appropriate technique (already available) is used.

It is worthwhile noticing here than another problem in the scope of fossil fuels is presently beginning to be also studied by adsorption microcalorimetry, namely the *porous texture of coals*. Coals are indeed being used in a variety of ways (combustion, gasification to synthetic natural gas, pyrolysis, liquefaction) whose improvement is directly dependent on our knowledge on porosity and on our ability to modify it. It happens that the largest portion of the surface atoms of coals are on the wall of micropores (d < 2 nm), especially molecular size micropores, whose characterization to-day is not yet satisfactory from the point of view of pore-size distribution, although progress has still been made these last years in the understanding of the micropore filling mechanism (Ref. 31). Nevertheless, since the adsorbate / adsorbent energy of interaction is appreciably enhanced by the narrowness of the pores, as shown by interaction potential calculations (Ref. 32), one may think of using adsorption microcalorimetry to characterize the micropores of coals. Interesting work has been recently carried out by *immersion microcalorimetry* into a series of normal alcohols (Ref. 33). The larger availability of micropores to the smaller molecules gives rise to a larger *specific* (i.e. related to the unit mass of adsorbent) enthalpy of immersion and also to a quicker phenomenon, because of an easier diffusion. Here, immersion microcalorimetry yields both a thermodynamic information (i.e. the enthalpy of immersion obtained by comparing the starting and the final state of equilibrium) and a kinetical information obtained in the meantime from the continuous calorimetric recording and which may be figured out, in its simplest form, in terms of "half-time of heat evolution". We think it worthwhile to complement such a work with gas adsorption studies (which may also be microcalorimetric, as was successfully done recently in the case of microporous charcoals (Ref. 34)) involving any "probe molecule" able to bring new information : nitrogen and argon (their comparison is always interesting, because of the permanent quadrupole moment of the nitrogen molecule whose size and polarizability are, on the other hand, similar to those of the argon molecule), carbon dioxide (at room temperature, it easily diffuses into the micropores), helium (the smallest available probe molecule) or oxygen (to characterize the potential reactivity of

a coal (Ref. 36)). More generally, once the reactivity of coals is concerned, one may think of a microcalorimetric study of the reactions taking place on their surface, following the lines of a number of successful studies of catalytic reactions by microcalorimetry (Ref. 37). Much systematic work, especially on well characterized "reference coals" is still necessary in this field.

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