INDUCED BIOCHEMICAL INTERACTIONS IN CRUDE OILS

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In the evolution of oil from sedimentary to reservoir conditions, the hydrogen to carbon ratios decrease while the oxygen, nitrogen, and sulfur to carbon ratios increase. During this process, the oils become heavier and richer in asphaltenes. In terms of chemical composition, the oils become enriched in resins, asphaltenes, and polar compounds containing the heteroatoms and metals. Over the geological periods of time, the chemical and physical changes have been brought about by chemical, biological (biochemical) and physical (temperature and pressure) means as well as by the catalytic effects of the sedimentary matrices, migration, flooding, and other physical processes. Therefore, different types of oils are the end products of a given set of such interactions which were brought about by multiple and simultaneous physiochemical processes involving electron transfer, free radical, and chemical reactions. A biocatalyst introduced into a reaction mixture of the type produced by such reactions will seek available chemical reaction sites and react at the most favorable ones. The rates and the chemical pathways by which the biocatalytic reactions will proceed will depend on the oil type and the biocatalyst(s). Some of the possible reaction pathways that may occur in such complex mixtures will be discussed.

Introduction

Chemical and physical changes which occur during the conversion of organic matter to oil under sedimentary and reservoir conditions have been studied extensively and reviewed in several classical works (for example 1 and 2). At the molecular level this conversion means chemical changes of many classes of organic compounds into a product containing saturated hydrocarbons (paraffins) and cycloalkanes (naphthenes), aromatic hydrocarbons including cycloalkane aromatics, resins, and asphaltenes. The latter are high molecular weight polycyclic compounds containing nitrogen, sulfur, oxygen, and metals. The relative concentrations of these compounds vary however, in terms of the crude oil, make up a unity which makes it a useful parameter for general comparisons of oils. All of these compounds are present in different oils which vary from light to heavy crudes with a broad spectrum of varying densities in which the conventional unit of gravity (API° gravity)[*] decreases or the oil becomes heavier, making this unit an important correlational factor. Additional general correlational factors describing different types of oils are the H/C ratios, which also decrease as the oil becomes heavier. Further, the polar N,S,O compounds become concentrated in the heavy ends of crudes. The heteroatom contents of these oils are measurable quantities and are also useful for correlational purposes. Thus, as the sulfur and nitrogen concentrations increase, the API° value decreases,

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[*] $gravity\ API^o = \dfrac{141.5}{specific\ gravity\ 60^o\ /\ 60^o\ F} - 131.5$

consistent with an increase in the concentrations of compounds containing heteroatoms and increasing molecular weights. The high molecular weight fractions also concentrate organometallic compounds.

Various combinations of these correlational units and others, such as isotope ratios and optical activity can be used for further characterization and classification of crude oils. In terms of the induced biochemical interactions, to be addressed later, several other crude oil characteristics will be discussed briefly. These include maturity and biodegradation of heavy crude oils.

Consider a petroleum reservoir as a reaction vessel containing hydrocarbons in a geochemically active matrix (liquid, gas, and solid phase) that is heated under pressure. Over geological periods of time, i.e. during the thermal maturation, such a reaction mixture undergoes many chemical reactions and chemical structure changes leading to a state of equilibrium, which at constant temperature and pressure, will be at a lower free energy state. Since the mixture contains organic molecules with many isomers, the most stable isomers will be those with the lowest free energy, such as paraffins at lower temperatures and aromatics higher temperatures. Thermal maturation favors hydrogen disproportionation reactions and degradation >C-20 compounds with an overall result of increase in API° gravity. The produced mature oil contains also a lower concentration of asphaltenes i.e. high molecular weight compounds containing heteroatoms N,S,O. Degradation due to sudden high temperature and pressure episodes has an opposite effect. It destroys paraffins and light oils, oxidizes oil fractions, and lowers the API° gravity. In extreme cases it can destroy the accumulated oil. Biodegradation is a particular case of degradation. This process results in (a) a volume decrease; (b) loss of n-paraffins, light aromatics, and naphtenes; (c) an increase in asphaltene contents and an increase in the concentration of N,S,O compounds and density, i.e. lowering of API° gravity. Generally the biodegradation of hydrocarbons under reservoir conditions proceeds via the following pattern: <C-20n-paraffins>isoparaphins>naphtenes>aromatics>polycyclic aromatics>isoprenoids, steranes, triterpanes. Single ring compounds are attacked before polycyclic compounds. The end result is a "heavy, biodegraded" crude oil. A "heavy immature" crude oil is an oil which has been subjected to regimes of either lower temperatures or shorter periods of time during "thermal maturation" of petroleum. In these oils chemical, physical, and biological changes, such as the presence of larger quantities of isoprenoids and terpenoids reflecting depositional conditions prior to significant heat effects are evident.

In a discussion dealing with either the formation of oils from the initial natural products, or the chemical and/or biochemical alteration of the end product, mention must also be made of isomers. It is well known that stereo isomers and positional isomers play decisive roles in chemical reactions. Some examples follow. The above mentioned n-paraffin's vs. isoparaphins reactions deal with the structural branching of hydrocarbons which under certain reactions, conditions may slow down or enhance a reaction. Stereochemical isomers dealing with configurational and conformational isomers, particularly important in olefinic and cyclic compounds influence both rates and yields of the products and finally the positional isomers such as found in heterocyclic compounds present in oils, add to the complexity of the reactions. Thus,

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in the group of nitrogen containing compounds called azaarenes isolated from oils (3) which vary from simple molecules, such as pyridine to larger tetraaromatic compounds, positional isomers of the heteroatom and a substituent offer multiple sites. A typical tetraaromatic azaarine, $C_{17} H_{11} N$ has 29 isomers, an addition of a methyl substituent results in 319 possible isomers. While, in most cases, only some isomers actually occur in nature, their effect on the chemical and biochemical reactivity has to be considered, particularly in the construction of large polymeric molecules leading to an end product such as a crude oil whose chemical composition affects the efficiency and the type of chemical and biochemical reactions.

Results and Discussion

Extensive studies conducted in this laboratory(4-6) of the chemical action of several biocatalysts on crude oils form California, Alabama, Arkansas, Wyoming, Alaska, Venezuela, and the Middle East have shown that biotreatment causes: (i) qualitative and quantitative changes in the light and heavy fractions of crudes; (ii) decrease in the asphaltene fraction with concurrent increase in the concentration of saturates, aromatics, and resins: (iii) decrease in organic sulfur and nitrogen content with concurrent biochemical conversion of polar compounds into lighter molecular weight components; (iv) decrease in the concentration of trace metals, e.g. V, Ni, As, Se, etc.

The biocatalytical reactions depend on the type of biocatalyst, the chemical composition of the crude oil, and the experimental conditions used. These reactions follow distinct trends which can be monitored by specific chemical markers who are integral constituents of crude oils. These include compounds containing sulfur and nitrogen, groups of hydrocarbons with characteristic mass fragmentation patterns and organometallic compounds. Typical results in which chemical markers have been used to monitor biocatalytic activity are shown in Table 1 and Figures 1 and 2.

Types of oil listed in Table 1 represent a wide range of heavy crudes. Thus, Venezuelan Cerro Negro (CN) and the Californian (M851) are biodegraded heavy oils. Californian oils (OCS and M836) are heavy because they are immature. Midway Sunset (MWS) is steam treated (secondary recovery), California heavy crude and, therefore, its chemistry has been altered by the treatment. In this case, an external agent has been introduced into the reservoir. The data presented in Table 1, show that a single biocatalyst acts with varying efficiencies on different crudes. Variations in the effects of a single biocatalyst on different oils have also been observed. In this case several biocatalysts have been used on the same oil (e.g. 5,6). Since the biocatalysts represent a select group of thermophilic microorganisms operating at ~ 65°C and above in bioreactors and defined experimental conditions which differ from those in the reservoirs, the treated oils should be considered as "biochemically converted," or bioconverted, rather then biodegraded. It is therefore recommended (4-7) to use the term "bioconversion" of crudes and their derivatives, rather then "biodegradation," a term referring to the action of indigenous microorganism, present in the oils which act under reservoir conditions over geological periods of time. The appropriateness of the term, is further supported by the action of biocatalysts on biodegraded oils, for example, CN and M851, where bioconversion by introduced catalysts

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occurs after biodegradation in the reservoir. Further, gas chromatographic/mass spectrometric analysis of the hydrocarbon distribution before and after biocatalytic treatment for different heavy crudes for example M851 a biodegraded, MWS steam treated, and OSC an immature (Figure 1) oil indicate a hydrocarbon distribution pattern in which an increase in the lighter hydrocarbon fraction occurs in the bioconverted oils. In this analysis, lighter hydrocarbons have shorter retention times. Similar results have been obtained consistently for other oils (e.g. 5,6 and references therein). Some of the observed "diagnostic properties" of chemical markers compare to those noted in the well known use of biomarkers for the determination of oil migration, maturation, biodegradation, rock source relationships, age, and depositional characteristics (8). Studies with biomarkers have also shown the need for the use of multiple markers for the description of a given process. The use of multiple markers appears to hold also in the evaluation of the biocatalyst activity such as, for example, the hydrocarbon distribution before and after the biocatalytic treatment of different heavy crudes. Compare M851, MWS, and oils (Figure 1, (e) (f)). Hydrocarbon distribution in OCS, relative to that in M851 and MWS, is not as distinctive. Additional analysis using sulfur and nitrogen chemical markers, shown in Figure 2, provides further spectroscopic evidence indicating a redistribution of compounds containing these heteroatoms. Because the experimental GC conditions were identical in all cases (amount of injected material, attenuation, gas flow, etc.) a direct qualitative and relative quantitative comparison is possible: there is a lowering in the overall concentration of heavy organosulfur and organonitrogen compounds. The latter is consistent with changes in the total S and N concentrations (Table 1). Further, organometallic compounds tend to concentrate in the heavy ends of crudes are also affected by the biocatalyst: the total metal content after the biotreatment decreases. Considering the total "chemical marker" information, an overall mechanism consistent with all of the current experimental evidence can be proposed (5,6,7). In the proposed mechanism, the introduced biocatalyst enters a mixture of colloidal, micellar, and molecular solutions containing many classes of compounds present in different concentrations in the crude, including the distribution of asphaltenes. It is a reasonable assumption that the formation of such "molecular solutions" begins with an asphaltene molecule (9,11), then proceeds to form three dimensionally stacked molecules to form a heavy crude "polymer," to micelles and super micelles to an end product cross linked with heteroatoms, metals, charge transfer complexes, free radical sites forming envelopes and clathrate type structures. A biocatalyst entering such a multifunctional mixture reacts with active sites initiating a dispersion of the colloidal, micellar and molecular solutions, ultimately resulting in a "depolymerization" type of a process by means of multiple inter- and intra- molecular reactions. This leads to a bioconversion of the crude in a manner in which the three dimensional, clathrate type structure gradually collapses with a simultaneous release of trapped hydrocarbons and a loss of heteroatoms to species soluble in the aqueous phase, leaving a product more amenable to the technology using chemical catalysts. Since the efficiency of both biocatalysts and chemical catalysts is influenced by the chemical composition of the starting materials and experimental conditions, it is reasonable to anticipate that the emerging technology based on the use of biocatalysts will be complimentary to the chemical processing of oils.

Acknowledgments

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**Table 1. Single Biocatalyst Effect on the Total
Concentration of Sulfur, Nitrogen, and Metals**

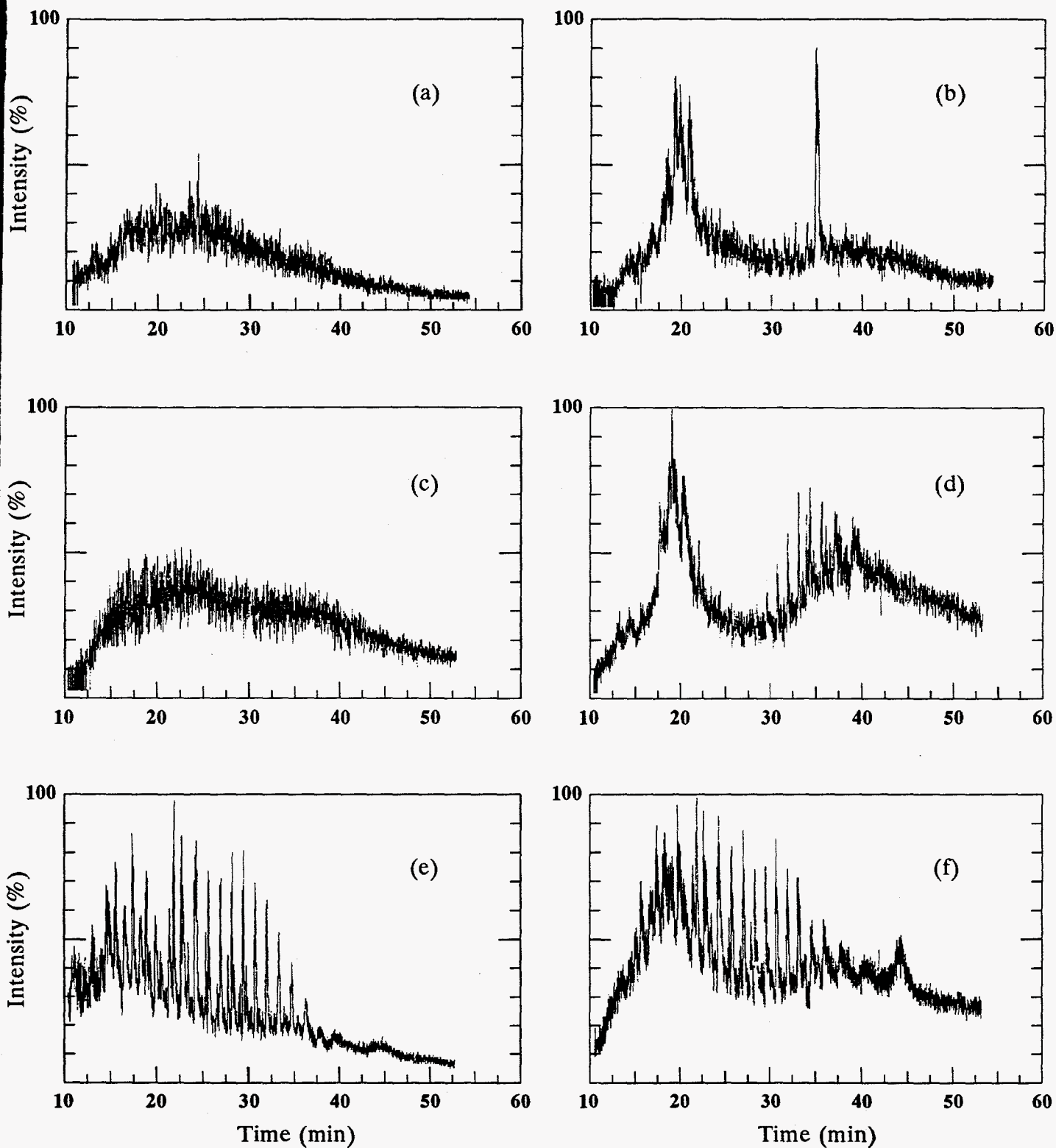| Oil	Biocatalyst Treatment	% Reduction in Sulfur	% Reduction in Nitrogen	% Reduction in Metals
CN	BNL-4-23	25	15	35(Ni), 58 (V)
MWS	BNL-4-23	50	15	25(Ni), 36(V)
OCS	BNL-4-23	45	45	20(Ni), 16(V)
M851	BNL-4-23	30	25	20(Ni), 22(V)
M836	BNL-4-23	25	25	14(Ni), 5(V)

Figure 1. GC-MS analysis. M/e57 gas chromatogram trace of M851, MWS and OCS crudes treated with BNL-4-23, (a) M851 control, (b) M851 treated with BNL-4-23, (c) MWS control, (d) MWS treated with BNL-4-23, (e) OSC control, (f) OSC treated with BNL-4-23.
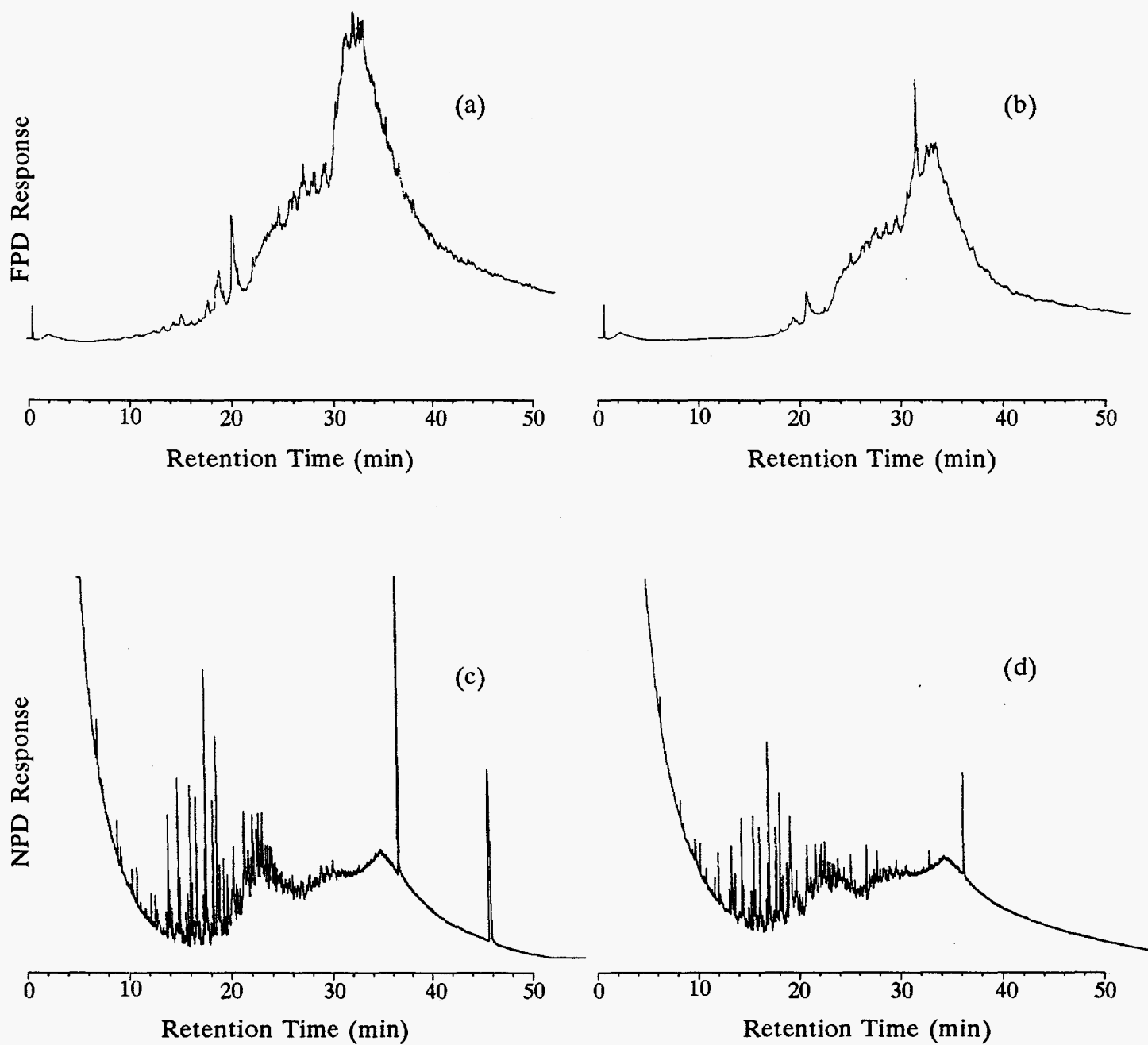
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Figure 2. Specific detector GC analysis of OSC, sulfur specific trace (Flame Photometric Detector FPD), (a) control and (b) OSC treated with BNL-4-23; nitrogen specific trace (Nitrogen, Phosphorous Detector, NPD, (c) control and (d) treated with BNL-4-23.