

A PETROGRAPHIC CLASSIFICATION OF SOLID RESIDUES DERIVED FROM THE HYDROGENATION OF BITUMINOUS COALS

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Introduction

Previous optical studies of coal dissolution have shown that the grain size of the organic constituents decreases with increasing reaction temperature (1, 2). These investigations were concerned mainly with chemical aspects of coal hydrogenation as a function of hydrogen transfer and thermal degradation; however no attempt was made to relate these parameters to the changing physical character of coal macerals. The "char" components produced during hydrogenation are known to be optically dissimilar to their original coal constituents. Therefore, it will be necessary to understand the physical mechanisms involved in maceral dissolution as well as the properties of these "char" or residue constituents before the chemical aspects of hydrogenation can be given adequate consideration.

A morphological characterization of solid residues will be a foundation for determining the various physical mechanisms involved in coal maceral degradation. Comparison of the petrography of a feed coal to that of its solid residue derived from hydrogenation is not sufficient for determining the origin of residue components. Understanding these origins, however, can be achieved by interpreting the progressive disintegration of coal macerals. These intermediate steps were observed in optical studies of residues produced by progressive batch hydrogenation and serve to associate the original feedcoal macerals to residue components derived from continuous-flow reaction.

Optical studies reveal that residue constituents are formed as a result of incomplete hydrogenation, repolymerization or carbonization. Those coal macerals which pass through the process unreacted or exhibiting only slight morphological alteration are readily identified. Other constituents are related to their precursory macerals by studying low temperature batch hydrogenation residues and are described on the basis of their morphology, relative reflectance, anisotropy, and grain size.

Sample Origin

Residues from two coal hydrogenation systems were used in this study. An experimental batch hydrogenation system utilized 20 g of minus 20 mesh coal with four parts by weight of tetralin in a stainless steel reaction vessel (nitrogen atmosphere). These preparations were reacted in a fluidized sand bath for three hours at a selected constant temperature in the range of 300°-450°C at 25°C increments (3). The reaction vessel contents were extracted in benzene and the resulting insoluble fraction was dried, embedded in epoxy resin, and polished.

The second system employed was a proprietary continuous-flow bench-scale reactor. This process used a feed rate of 400 g/hr of minus 200 mesh coal slurried in a 1 to 3 ratio with solvent-recycle or anthracene start-up oil. The slurry was pumped under a pressure of 1500 psig into a reaction column with hydrogen. Reported reaction temperatures of 441°C and 427°C were given for a residence time approximating 30 minutes. Filtration was conducted at regular intervals to determine the product balance for each run. Filter cake materials were extracted in pyridine and the resulting residue was dried, embedded in epoxy resin, and polished.

Solids from a pilot plant continuous-flow reactor were also subjected to optical observation.

Comparative Optical Results

The petrography of feed coals used for conversion in these hydrogenation systems are summarized in Table I. The more reactive coal constituents, vitrinite and exinite (see Fisher *et al.* (4) and Davis *et al.* (5)) appear in varying concentration. The reactive maceral content of the Indiana #6, West Kentucky #14, and Illinois #6 feed coals are relatively high while those for the Indiana #1 Block and the Australian Callide feed coals are substantially lower. These feed coals are high volatile bituminous in rank with the exception of the subbituminous A Callide seam.

Vitrinite Contributions to Residues

Table II presents the proposed residue classification and disassociation mechanisms which link the residue components to their original macerals. The most diverse contribution to hydrogenation solid residues is obtained from vitrinite. The fact that this maceral exhibits a capacity to swell or contract within the temperature range of liquefaction is well documented. However, the appearance of unreacted vitrinite in these residues may present an inconsistency with the properties of vitrinite in the temperature range of liquefaction. Plate I, Figure (a) shows a particle of vitrinite containing a spore exine (sporinite) remaining in continuous-flow hydrogenation after reaction of the West Kentucky #14 feed coal at 441°C. Typically, vitrinite that may be distinguished in these residues shows some thermal contraction or expansion along bedding planes. However, the particle illustrated here attained only a slight granularity along one of its edges. The incomplete hydrogenation and apparent lack of thermal degradation of vitrinite suggests that reported reaction temperatures may not be accurate.

Plate I, Figure (b) shows two additional vitrinite-residue components formed as reaction temperatures increase to 350°C in the batch hydrogenation of the Indiana #1 Block feed coal. The appearance of a spherical morphology which is here called "vitroplast", [vitro - derived from vitrinite, refers to the original material and plast - derived from plasty (a combined form meaning from the Greek *plastos*, formed and *plassein*, to mold)] and a submicron material which will be assigned to the "granular residue" category are depicted in Table II. The term "vitroplast" describes a plastic or once-plastic thermal degradation product of vitrinite. It is characterized by flow-structure as well as the spherical morphology seen in Plate I, Figures (b), (d), and (e). Vitroplast also appears as broad (>100 μ) isotropic areas containing inclusions of other residue components and as angular fragments. Its identification is often difficult due to its gradual transition to semi-coke.

The dissolution of vitrinite during hydrogenation is demonstrated by Plate I, Figure (c). The batch hydrogenation of the Indiana #6 feed coal at 325°C exhibits the transition from slightly thermally altered vitrinite to the vitroplast flow structure and spherical morphology referred to above. The lower reflectance of vitroplast is an indication of the disruption of the vitrinite lamellae and the resulting amorphous crystallography. Vitroplast formation may also occur during continuous-flow reaction, an example of which is illustrated in Plate I, Figure (d) (West Kentucky #14 residue at 441°C).

The granular residue seen in Plate I, Figure (b) is submicron in size (0.3-1.0 μ), approximately spherical in shape, and appears blue and red in polarized reflected light. Its appearance on the surface of vitrinite during progressive hydrogenation resembles the genesis of micrinite from weakly reflecting vitrinite during metamorphic coalification as discussed by Teichmüller (6). Qualitative electron microprobe analyses of the submicron constituents from the continuous-flow residue of Illinois #6 coal indicate that approximately 11 percent of the particles tested were organic.

The remainder of the granular residue is consequently assumed to represent fragments of finely dispersed clay. More work is required before compositional differentiation of the submicron fraction can be achieved.

The continued degradation of vitrinite and the spherical vitroplast derived from it is seen in the development of "cenospheres". This term was first applied to structures formed as a result of rapid heating of pulverized coal by Newall and Sinnatt (7) and later by Street *et al.* (8). Cenosphere is a morphological term defined as a reticulated hollow sphere composed of ribs or frames and windows. In hydrogenation residues simple cenospheres are often observed which lack reticulate texture and the thin membranes or windows. These less complex structures are observed in the continuous-flow residue of the West Kentucky #14 feed coal (Plate I, Figure (d)). Simple cenospheres are seen in close association with the spherical vitroplast, and exhibit related morphologies. This association may be observed for more complex cenospheric structures. Plate I, Figure (e) suggests the development of gas bubbles in the interior of a vitroplast sphere from the continuous-flow residue of West Kentucky #14 coal (427°C). While in the plastic state, gases formed by thermal cracking exert sufficient pressure to cause expansion and eventually lead to the formation of a highly reticulate hollow sphere as seen in Plate I, Figure (f).

Optical observation reveals that as vitrinite is subjected to increasing reaction conditions it may swell and become plastic, forming both a fine-grained residue fraction, inert to further hydrogenation, and a plastic, low-viscosity phase (vitroplast) which is immiscible in the hydrogen-donating solvent. The granular residue constitutes a major portion (>50%) of these residues and may be considered as a semi-quantitative category composed of both inorganic and organic constituents. The vitroplast is more variable in concentration, much like the "unreacted vitrinite" category. Quantitative data will be required to distinguish whether these varying concentrations are due to characteristics of the feed coal or to the reaction conditions.

Vitroplast may not be as reactive to further hydrogenation as unaltered vitrinite, especially when the vitroplast's reflectance increases above that of the precursor vitrinite. The spherical vitroplast generally exhibits reflectances above 1.0 percent, although the reflectance level is variable. Presumably, the immiscibility of the disoriented vitrinite lamellae and a subsequent loss of internal pore structure makes hydrogenation increasingly difficult. A continued increase in temperature may affect the spherical vitroplast, causing internal thermal cracking and expansion to form cenospheres.

During hydrogenation repolymerization of the vitrinite-derived liquids may occur as a result of hydrogen starvation, temperature or pressure drops, or a critical accumulation of solids. This observation is confirmed by the presence of semi-coke formed specifically by the mesophase mechanism. Mesophase is a transient intermediate stage between a unique fluid system (liquid crystals) of high molecular weight and a solid anisotropic carbon such as semi-coke (9). The initial appearance of mesophase can be an anisotropic sphere formed by the lamellar stacking of the liquid-crystal polymers parallel to the sphere's equator. A slight increase in temperature can result in this transient phase being converted irreversibly into semi-coke. A second mode of occurrence of mesophase which is of greater significance to liquefaction processes is the adsorption of nematic liquid crystals on inert surfaces. Marsh *et al.* (10) have shown that liquid crystal (mesophase) development can occur in the carbonization of some coals and coal tar pitches, suggesting that during liquefaction, coal-derived substances can repolymerize to form liquid crystals.

The potentially deleterious effects of nematic liquid crystal nucleation during hydrogenation is seen in Plate II, Figure (a). During a continuous-flow pilot plant reaction of an Illinois #6 feed coal, liquid crystals are shown to have formed in concentric layers on the surface of an inert particle. Whether polymerization occurred

at the surface or within the surrounding fluid can only be speculation. However, as a result of lamellar stacking and subsequent development of cross-link bonding, an anisotropic nucleated carbon is formed which is inert to further hydrogenation. The development of this phase has been associated with reaction vessel coking problems.

Liptinite Contributions to Residues

The liptinite group of macerals includes sporinite, resinite, cutinite, and alginite. Of these, sporinite appears in low concentrations in high volatile bituminous coals. Due to the very minor concentrations of the other liptinite components, a systematic study will not be covered here.

Teichmüller (6) suggests that micrinite forms from sporinite and other liptinite macerals during the metamorphosis of coal. She contends that the genesis of spore-derived micrinite occurs only during the high volatile bituminous stage of coalification. This suggests the possibility that sporinite may break down into a granular residue constituent as well as liquid by-products during hydrogenation. Plate II, Figure (b) exhibits a megaspore exine from the Indiana #1 Block coal which, as indicated by its porous and granular surface, may be forming this granular material during the course of coalification. Plate II, Figure (c) is a photomicrograph of the remains of a microspore after batch hydrogenation of the same feed coal at 375°C. A high reflecting granular material is observed along its swollen and partially reacted central cavity. One implication is that during hydrogenation of high volatile bituminous coals, a submicron granular material may be generated from sporinite to become a possible addition to other inert constituents.

Inertinite Residue Contributions

The group of coal macerals known as inertinite includes fusinite, semifusinite, macrinite, and micrinite. Their inertness relative to other macerals was determined through their behavior in carbonization; however, the term "inert" does not adequately describe their properties. These macerals are considered by some to be semi-inert even in coke making (11) and the same may be true for liquefaction.

The classic study by Fisher *et al.* (4) and later work by Davis *et al.* (5) indicate that fusinite is less suitable than the other "inertinites" for hydrogenation and may in fact be totally inert during liquefaction. It is observed in moderate concentration in hydrogenation residues and is generally more abundant than in the original feed coal. The difference in fusinite concentration is a result of continuous circulation, mechanical abrasion, and accumulation in the turbulent flow of continuous-flow reactors. Fusinite is usually readily apparent in its dispersed form as high reflecting angular fragments which often exhibit remnant cell structure.

Semifusinite is transitional in reflectance, morphology, and chemistry between vitrinite and fusinite. The partial reactivity of semifusinite has been assumed for carbonization, and may be valid for the liquefaction process. The Australian Callide seam which has an unusually high concentration of semifusinite (Table I), was reacted in the batch hydrogenation system to investigate semifusinite's partial reactivity. The coal gave a 40 percent conversion at 400°C indicating the probability that components other than vitrinite and exinite were involved in the reaction. Optical examination of the Callide residue substantiated the partial reaction of semifusinite. Plate II, Figure (d) shows semifusinite with slightly rounded edges and irregularly shaped cell lumens which may have begun to close when the structure became plastic. The residue also contains a high concentration of spherical vitroplast. Since this coal has a very low vitrinite content, and noting the close association of the vitroplast with the plasticized semifusinite, it seems likely that this vitroplast has been derived from semifusinite. However, it is not possible to make a definite inference as to the source of the vitroplast. At this stage of research, the reactivity of semifusinite must be determined by empirical testing for individual coals.

Another coal constituent which is considered to be inert during carbonization is macrinite. Table I reports a high percentage of this component in the Indiana #1 Block feed coal. Batch hydrogenation of this sample at 450°C resulted in a 72 percent conversion, indicating again that some of the "inert" constituents must have reacted. Microscopic observation of the progressive reaction residues suggests that with increasing temperature, macrinite reacts and that by 425°C no distinguishable residue analog remains. By adding macrinite to the reactive constituents (vitrinite and exinite, Table I) the percentage of reactive macerals now closely corresponds to the 72 percent total conversion. As with semifusinite, the relative reactivity of macrinite must be determined empirically for each feed coal.

Another constituent present in low concentrations in this series of high volatile bituminous coals is micrinite. Due to its fine grain size (0.1-1.0 μ), progressive hydrogenation is difficult to assess. There are physical similarities between micrinite and the granular material produced by the degradation of sporinite and weakly reflecting vitrinite during hydrogenation. However, it is not known whether there are any chemical similarities which could account for micrinite's reaction during liquefaction. As with the other members of the inertinite group, micrinite's partial reactivity must be determined empirically for each individual feed coal.

Carbonized Residue Constituents

The development of anisotropy in the insoluble organic constituents of hydrogenation can be extensive. Any one of the residue components described above can develop anisotropic domains and, at the same time, retain a distinctive and characteristic morphology. The cenosphere in Plate I, Figure (f) is an example. The outer wall has been carbonized to a fine-grained anisotropic mosaic. Similarly, vitroplast may develop an anisotropy depending on temperature and time. The distinction between this type of semi-coke and that produced specifically as a result of a liquid crystal formation is important, although both types of semi-coke represent a loss of reactive constituents and repolymerization. The appearance of these carbonized particles may indicate that reaction conditions were too severe, or that reactor flow was not efficient and that these particles were subjected to a longer residence time than reported.

Summary and Conclusions

It is evident from the preceding discussion that, as a result of optical studies of the residues obtained from progressive batch hydrogenation, insight is gained into the origin of residue components from continuous-flow liquefaction. The result of these optical studies is a classification of organic solid residues (Table II), and some understanding of the physical disintegration of coal macerals. Optical observation of these residues can also provide an alternative method of analyzing run conditions and determining product balance for continuous-flow systems.

The chemical heterogeneity of coal macerals and the various mechanisms by which these macerals disintegrate are reflected in the morphologies and phases observed in the insoluble residues. The fact that vitrinite is a complex organization of different cross-linked polymers may account for the formation of vitroplast and cenospheres rather than the slightly altered vitrinite. Optical examination of coal indicates that there are slight differences in reflectance and morphology between vitrinitic particles within the same sample. The partial reactivity of semifusinite for some coals is a further demonstration of the effects of chemical heterogeneity.

Diversity of thermal environments during liquefaction is definitely reflected by these residues. The appearance of unreacted or slightly altered vitrinite implies that thermal conditions are too low. In contrast, the occurrence of semi-coke or the development of anisotropic domains suggest more severe conditions. The variation

in reflectance of the vitroplast spherical morphologies (Plate I) may indicate that reaction temperatures are variable. The lower reflecting spheres apparently have been less thermally altered than those of higher reflectance.

Further, the classification indicates several constituents which may affect the efficient operation of continuous-flow liquefaction processes. Besides liquid crystal (mesophase) nucleation being responsible for coking during reaction, the spherical vitroplast and cenosphere components are also a potential problem. Increased concentration of these phases could detrimentally affect filtration. Their nearly spherical shape could lead to a very tight packing during filtration, resulting in decreased filtration rate.

The potential of residue microscopy is not yet fully realized. However, by classification of the organic and inorganic constituents, a means of systems product balance may be developed. Comparison of quantitative point-count data derived from this classification should also aid in determining the "optimum-yield" run conditions.

Acknowledgments

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TABLE I
PETROGRAPHIC ANALYSIS OF FEED COALS

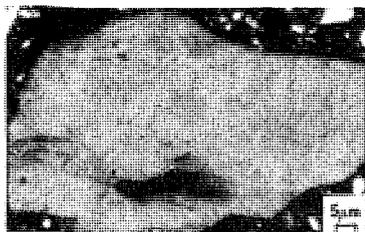
Sample No.	Method of Hydrogenation	Seam	State	Macerals, Vol. %							
				Vit.	Fus.	Sf.	Mac.	Mic.	Ex.	Res.	Cut.
PS0C-106	Exp.*	Indiana #1 Block	Ind.	25	10	12	21	6	23	2	1
PS0C-280	Exp.	Indiana #6 Seam	Ind.	92	1	1	0	3	2	1	0
PS0C-303	Exp.	Callide Seam	Queensland, Australia	15	4	73	1	2	2	0.2	3
POC-288	Continuous-Flow**	W. Ky. #14 Seam	Ky.	74	3	5	3	13	2	0	0
POC-289	Continuous-Flow	Ill. #6 Seam	Ill.	91	5	2	0	1	1	0	0

* Experimental batch-hydrogenation
 ** Continuous-flow reaction

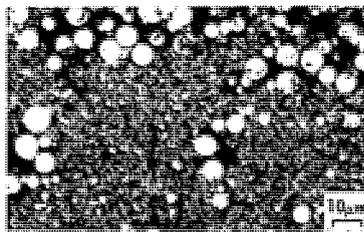
Vit. - vitrinite Sf. - semifusinite Mic. - micrinite Res. - resinite
 Fus. - fusinite Mac. - macrinite Ex. - exinite Cut. - cutinite

TABLE II
BEHAVIOR OF COAL ORGANIC CONSTITUENTS DURING LIQUEFACTION

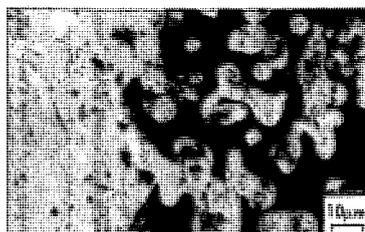
Maceral Precursor	Disassociation Mechanisms	Organic Residue Components
Vitrinite	Slightly altered vitrinite (contracted and/or swollen) Granular residue Vitroplast (high molecular weight) → cenosphere Vitroplast (intermediate molecular weight) → vitroplast Hydrogenated Product (repolymersized) → liquid-crystal ± mesophase → semi-coke	Unreacted vitrinite Granular residue Cenosphere Vitroplast Semi-coke
Fusinite	No observable mechanism	Fusinite
Semifusinite	Possible fractional contribution, mechanism similar to vitroplast	Semifusinite or semi-coke
Macrinite	Possible fractional contribution, mechanism unknown	Unknown
Exinite	Fractional contribution of submicron granular material	Granular residue



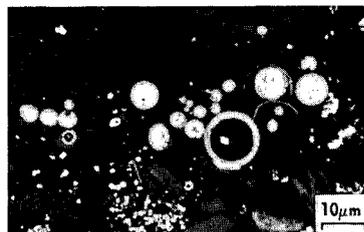
(a)



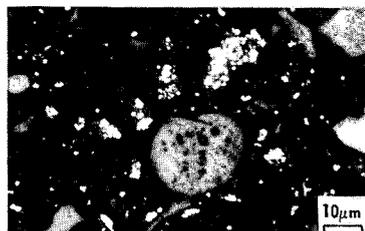
(b)



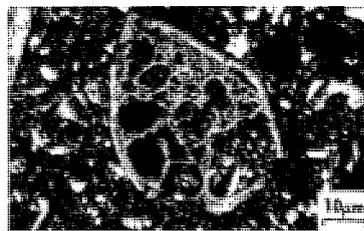
(c)



(d)



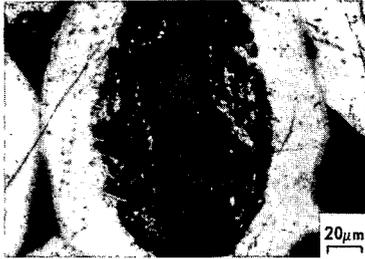
(e)



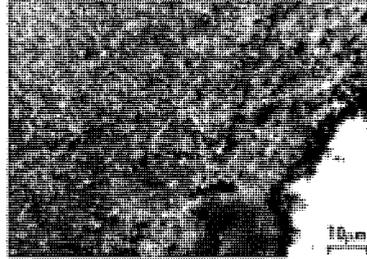
(f)

PLATE I: PHOTOMICROGRAPHS OF HYDROGENATION RESIDUES

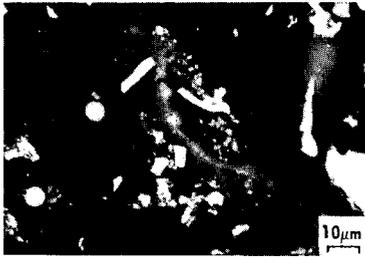
- Figure (a). Unreacted vitrinite containing sporinite from continuous-flow reaction of the West Kentucky #14 (441°C).
- Figure (b). Vitroplast and granular residue produced in batch hydrogenation of Indiana #1 Block at 325°C.
- Figure (c). Vitrinite plasticity and the formation of vitroplost at 325°C, after batch hydrogenation of Indiana #6 seam.
- Figure (d). Vitroplast and a simple cenosphere in the West Kentucky #14 residue (441°C, continuous-flow reactor).
- Figure (e). Vitroplast exhibiting gas bubble generation as a prelude to cenosphere formation. Continuous-flow reaction of West Kentucky #14 (427°C).
- Figure (f). Highly reticulate cenosphere with carbonized outer wall. Continuous flow reaction of the West Kentucky #14 at 441°C.



(a)



(b)



(c)



(d)

PLATE II: PHOTOMICROGRAPHS OF HYDROGENATION RESIDUES

- Figure (a). The effect of liquid crystal (mesophase) nucleation on calcite causing semi-coke formation. Pilot plant continuous-flow reaction of Illinois #6 feed coal at 446°C.
- Figure (b). Sporinite observed in the Indiana #1 Block feed coal, showing signs of disintegration during normal coalification.
- Figure (c). Remnant microspore exhibiting granular residue formation in the 375°C batch hydrogenation residue of the Indiana #1 Block.
- Figure (d). The apparent plasticity and partial reaction of semifusinite from the 400°C batch hydrogenation run using the Austroliion Callide seam.