

STRUCTURAL INSIGHTS TO HEAVY RESID AND COAL FOR DESIGNING UP-GRADING

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Objectives and Approaching of Resid Up-grading

Increasing demand for transportation fuel of higher performance and less environmental load and increasing dependence on heavy crude, resid, and coal require the development of more efficient up-grading technology in coming future. Several processes have been practiced for up-grading, which consists of depolymerization, aromatic hydrogenation and ring opening, metal and heteroatoms removals. The degrees of reaction severity varied the yield and quality of the product, charging the responsible cost. Such reactions are derived thermally and catalytically according to the severity of design and cost/performance balances.

Thermal up-grading is usually cheap in facility and running cost, but suffers the limited conversion, and selectivity to wanted products, insufficient quality of product and unwanted coke. Some coke can be designed to be the product of high quality such as those for blast furnace and electrode. Handling of solid coke is often energy-loss, dirty and tedious.

Catalytic process can drive the reactions as wanted, although the deactivation contaminants, and poisoning of the catalyst limit the advantage of the process, increasing the catalyst cost. Sometime cheap catalyst is obliged to use because of limited turn-over number and use of repetition. Combination of thermal and catalytic processes has been designed to optimize their advantages.

The design of up-grading is to define the reactions needed to convert the resid to transportation fuel, the best catalysts for the respective reactions, their optimum use and recovery for their repeated use. Hence the chemistry on the structural changes of organic substrates, catalyst surface, and active species should be described in details as much as possible.

Structural Images of Resid, especially Significance and Liberation of Molecular Assembles

Resid has been described as polyaromatic, polynuclear polymers. The aromatic rings are connected directly (aryl-aryl linkage) or through methylene bridges to form polynuclear chains, carrying heteroatoms within the ring and alkyl substituent on the rings as imaged from the structure of depolymerized units. The alkyl chains in the substituents are basically normal and very long up to 30-40 carbons. The hetero-cyclics such as pyrrole, pyridine, and thiophenes carry heavy metals such as vanadium and nickel as observed in porphyrins.

The primary polyaromatic polynuclear chains form three dimensional network through the non-covalent as well as covalent linkages. The non-covalent bonds link the chains through alkyl chain entanglement, π - π stacking of aromatic rings, acid-base or hydrogen bonding, coordinative bridge of the metal cations, and charge transfers among the heterocyclic rings. Such intermolecular assemble sometime forms micelle, influencing strongly the solubility in the matrix of smaller partners and reaction solvent and reactivity through governing the contact of the

reactive sites with the reagent as well as active site on the catalyst, and favoring the intermolecular condensation.

The asphaltene in the resid which is defined by the solubility in hexane and benzene is a target of up-grading. Its coking/fouling reactivity, inertness for depolymerization and tendency for phase separation and precipitation are ascribed to the structure of its chains and their intermolecular assembles. Liberation of molecular assemble by breaking intermolecular linkage through solvation, ring hydrogenation, removal of bridging cations and heterogroups. Such liberation enhances solubility and the reactivity for depolymerization, reducing the coking reactivity and irreversible adsorption.

Detection of Molecular Assemble

Molecular assemble in resids and coals has been accessed by XRD, NMR and ESR through diffraction of aromatic stacking, different relaxation and rotational narrowing of metal porphyrins, respectively. XRD of slow step scan provides two broad diffraction peaks at 20° (γ -band) and 26° (π -band), receptively, which are believed to reflect alkyl entanglement and π -stacking. Figure 1 illustrates XRD profiles of a vacuum residue and its fractions. The intensity of π -band increases in the order of saturate, aromatic, polar, and asphaltene fractions, indicating increasing significance of π - π stacking. In addition to two broad bands, very sharp peaks are observable at 22° and 24° , which are attributable to n-paraffin's crystals.

Liberation of Molecular Assemble

High temperature and solvents moderate both stacking. Higher temperature reduced the π -stacking and shifted γ -band to the lower angle. Figures 2 and 3 show XRD of VR in toluene and swollen Beulah-Zap coal by DMF and THF. Both bands of VR were weakened according to the amount of solvent although the γ -band reduced its intensity more rapidly. In contrast, solvent swelling of coal appears to moderate the π -stacking more selectivity.

Removal of cationic bridges in coal liberates the aliphatic entanglement in the coal producing weaker hydrogen bond.

Extraction and Adsorption of Asphaltene

Asphaltene in the VR is the target of conversion while it is a troublemaker in the catalytic conversion. Hence its removal prior to the up-grading of heavy resid is an approach to avoid the trouble. Asphaltene can be selectivity extracted by liquid propane under supercritical conditions.

Some carbon materials adsorb asphaltene rather selectively. Their pore must be larger than 10A. Carbon blacks of nanoparticulate adsorb selectively the asphaltene at a high capacity. Selective and deep removal of metals in VR is most wanted since the demetalation is the first step in a series of hydrotreatment stages, where the capacity of demetalation agent and its completeness govern efficiency of the process.

Inflence of Hydrotreatment on Molecular Assemble

Hydrotreatment produces distillate and more saturate, converting the polar and asphaltene fractions. Aromatic rings are hydrogreated and polymer chains are broken down by such treatment. Hydrogenation reduces intensities of both γ and π bands.

Configuration and Catalyst for Hydrotreatment of Resid and Coal

Hydrotreatment consists of metal removal, hydrogenation, hydrocracking, hydrodesulfurization and hydrodenitrogenation. Hydrogenation is believed to moderate the coking and sludge formation and enhances the reactivity for cracking. Since the hydrogenation favors thermodynamically the lower temperature, while the cracking does higher temperature. The active catalyst is preferably used at a separate step of lower temperature for the pretreating hydrogenation.

Aromatic and hydrogen donor solvents often help the hydrotreatment by dissolving heavier components and suppressing on retrogressive reactions. Dry sludge produced in the hydrocracking is successfully suppressed by the two stage hydrocracking and added solvent to achieve a high distillation yield.

Catalysts of fine particles are appreciated in the moving bed hydrotreating. Recovering and repeated use as well as penetration into micelle or coal grain are concerned. Carbon black of nano-particles is a candidate support to solve the problems. NiNo/carbon black has been reported to give the very high activity for coal liquefaction NiFe/carbon black shows comparable activity, although its activity for ring hydrogenation is limited, requiring donor solvent in the liquefaction.

Unfortunately such catalysts adsorbs strongly the asphaltene to be insoluble during the hydrotreatment. Some modification of the support is necessary to reduce its surface polarity for limited adsorption, maintaining the dispersion form against sulfide active species.

Molecular Identification of Gas Oil and Vacuum Gas Oil for Desulfurization and Denitrogenation

Gas chromatograph equipped with atomic emission detector can separately identify hydrocarbons, sulfur, nitrogen, oxygen and even metal containing species. Molecular separation by a suitable column and every identification are now in progress. Nevertheless the reactivity of the respective species inhibiting and deactivation factors of partner species are measured very easily. Figure 4 illustrates typical chromatographs of hydrocarbons, sulfur, nitrogen and oxygen species in the coal derived gas oil. Analyses before and after the hydrotreatment tell us their reactivity. Some intermediate products are also identified to establish the reaction scheme in the presence of competitors and inhibitors in the same oil.

The desulfurization schemes of its most refractory 4,6-dimethyldibenzothiophene have been proposed as shown in Figure 5. Based on the scheme, natures of the active site and inhibitors are identified and better catalyst and reaction configuration can be designed. Denitrogenation of nitrogen species in the gas oil is studied by the same approach.

Another significance of the molecular identification is that the products in the hydrotreated resid suggest us the unit molecular structure of the building blocks of the polymeric substances.

Aromatic Ring Opening

Heavy feed and coal tend to yield highly aromatic products. Aromatic rings are hopefully opened into alkylnaphthenes for clean and efficient combustion. Selective hydrogenation of aromatic ring by noble metal catalyst and selective C-C bond fission by adequate zeolite catalyst appear most promising. Pore, crystal sizes, and crystallinity of the wall and zeolite content in the synthesis are necessary to be improved.

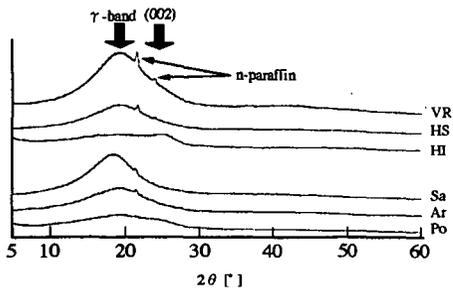


Figure 1 XRD of AM-VR fractions (Step Scan 4 sec. / 0.01°)

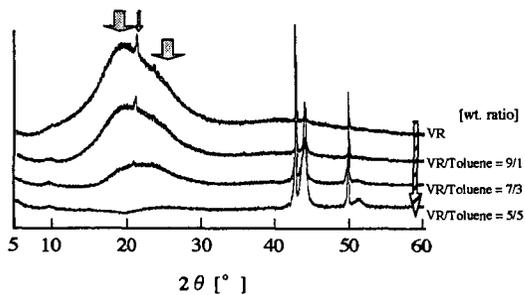


Figure 2 XRD of VR in toluene (Step Scan 4 sec. / 0.01°)

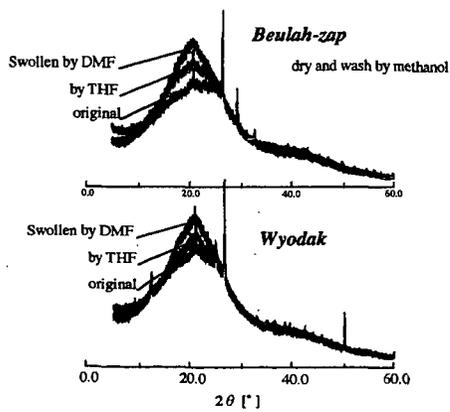


Figure 3 XRD of Swollen coals with DMF and THF (Step Scan 3 sec. / 0.01°)

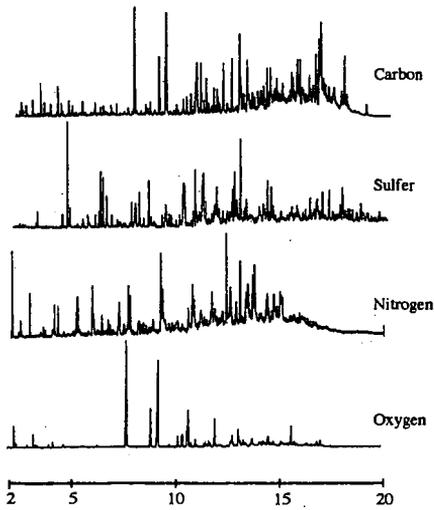


Figure 4 GC-AED chromatograms of C, S, N, O species in South Banko Coal Liquids

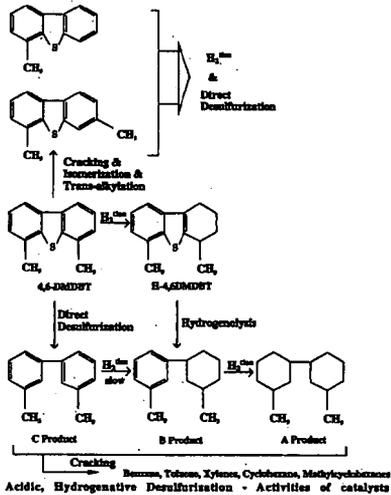


Figure 5 Hydrodesulfurization Reaction Schemes for 4,6-Dimethyldibenzothiophene