

## CHALLENGES IN THE PROCESSING OF PETROLEUM SUPPLEMENTS

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Research and development work in the conversion of coal, of the kerogen in oil shale, and of the tar from bituminous sands to petroleum supplements has been a periodic phenomenon in the United States. During each period of intense effort major technical improvements have been made. Current research efforts have succeeded in bringing the cost of gasoline from these supplemental hydrocarbons much closer to the cost of gasoline from petroleum. One of the important factors which brings the cost closer is the increased cost of discovering and producing new petroleum reserves. Large scale commercial utilization of petroleum supplements will occur when the cost curves meet.

Historically, coal conversion research has been done largely by chemists and engineers employed in the coal industry, in government research laboratories or in research institutes. Only within the last few years has the petroleum industry seriously committed itself to studying production of liquids from coal, oil shale and bituminous sand. Earlier work in the petroleum research and development laboratories had been concentrated on petroleum feed stocks whose character is quite different from the liquids obtained from pyrolysis of other hydrocarbons.

Differences between the more familiar petroleum and the liquids produced from coal, oil shale and bituminous sands lie in the areas of; (1) oil composition, (2) the analytical techniques used in characterizing each material, (3) associated minerals, and (4) variations due to processing.

### OIL COMPOSITION

Between the time of initial formation of petroleum and its migrating to and being trapped in the structure from which it is produced, any thermodynamically unstable molecules have undergone reaction or have been adsorbed or filtered from the bulk of the stable hydrocarbon constituting the final, presently produced petroleum. The liquids obtained from pyrolysis of coal, oil shale, and to a lesser degree, tar sands, on the other hand contain many very reactive hydrocarbons and heterocyclic compounds. The properties of the liquids produced during pyrolysis change appreciably over very short time periods due probably to condensation and polymerization reactions. This has been observed by many research groups who have noted that an initially light colored, very fluid, low pour point product from pyrolysis of oil shale or of coal darkens during the first few hours after distillation.

Both the pour point of the liquid and the viscosity increase noticeably after its production. Preliminary work in our laboratory indicates that the changes that occur are very sensitive to the presence of oxygen. They are apparently not photosensitive as had been earlier assumed. Nonetheless the changes are marked and will require either rapid subsequent processing of the liquid or a stabilization step to prevent the decrease in quality of the petroleum supplement.

#### ANALYTICAL TECHNIQUES

Another difference that petroleum refinery scientists and engineers must become aware of lies in the different types of analyses that have been developed for each of the potential petroleum substitutes.

Coal traditionally is characterized by "proximate analysis" and by "ultimate analysis". The proximate analysis comprises determinations of moisture, volatile matter, ash, and fixed carbon (the last by difference). With it is usually included a determination of sulfur and sometimes phosphorus. While the proximate analysis is the most widely used method for analyzing coals it is of little value in predicting convertibility of the coal to a petroleum supplement. Ultimate analyses are elemental analyses and take much longer to perform than the proximate analysis. Considerable technical skill is required and this analysis has not usually been done in coal plant operations.

Table 1. CHEMICAL COMPOSITION OF SOME COALS AND PETROLEUM

	Anthracite	Medium volatile bit.	High volatile A bit.	High volatile B bit.	Lignite	Petroleum Crude
C	93.7	88.4	84.5	80.3	72.7	83-87
H	2.4	5.0	5.6	5.5	4.2	11-14
O	2.4	4.1	7.0	11.1	21.3	
N	0.9	1.7	1.6	1.9	1.2	0.2
S	0.6	0.8	1.3	1.2	0.6	1.0
H/C atom ratio	0.31	0.67	0.79	0.82	0.69	1.76

Coal analysis on moisture and ash-free basis.  
Ash content of coal 3 to 15%

G. Alex Mills, Industrial and Engineering Chemistry, vol. 61, No. 7,  
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Table 1 gives the ultimate analyses and hydrogen to carbon atom ratio of some coals and of petroleum. From the table we note that the hydrogen content of those coals most suitable for conversion into petroleum supplement by hydrogenation distillation, namely high volatile bituminous coals is in the range 5.5 percent. Petroleum on the other hand will contain from 11-14 percent hydrogen. Distillates from coal contain up to 9 percent hydrogen. Current technological methods for producing liquids from coal are based on the concept that the hydrogen rich components should be distilled from the coal and used as a petroleum supplement. The char or coke residue might better be used as a fuel rather than attempting the difficult task of converting the whole coal to hydrocarbons.

Table 2. HYDROGEN TO CARBON ATOM RATIO OF PETROLEUM AND SUPPLEMENTS

<u>Material</u>	<u>H/C Atom Ratio</u>
Texas Crude	1.55
Pennsylvania Crude	1.95
Bituminous Tar	1.75
Shale Oil	1.48
Coal Tar	1.32
Benzene	1.00
Toluene	1.14
Iso-octane	2.25

In Table 2 are listed the hydrogen to carbon ratios of typical petroleum supplements, of some pure hydrocarbons of value in gasoline, and of some Texas and Pennsylvania crude oils. Iso-octane has a hydrogen to carbon ratio of 2.25; a typical Pennsylvania crude oil high in paraffin content has a ratio of hydrogen to carbon of 1.95; a crude oil from Texas has a hydrogen to carbon ratio of 1.55, a typical bituminous tar has a ratio of 1.75, shale oil 1.48 and a straight coal tar distillate 1.32. The hydrogen to carbon atom ratio in a high volatile bituminous coal is 0.82. Included in the table are benzene and toluene, major components of coal oils, which have a hydrogen to carbon atomic ratio of 1.00 and 1.14.

There are two things of importance to note from these tables; first, the significantly higher hydrogen content of oil from coal compared to the original coal, and second, the hydrogen deficiencies compared to paraffinic crudes.

One compensating factor to be kept in mind is that relatively high percentages of the hydrocarbons in the coal liquid are aromatic. The final hydrogen to carbon ratio of a gasoline from coal could probably be in the range 1.4 to 1.5.

Table 3. ULTIMATE ANALYSES

	<u>Bituminous Tar</u>		<u>Shale Oil</u>		<u>Coal Tar</u>	
	<u>Wt.%</u>	<u>Atom%</u>	<u>Wt.%</u>	<u>Atom%</u>	<u>Wt.%</u>	<u>Atom%</u>
H	10.4	10.4	10.43	10.43	9.1	9.1
C	83.3	6.94	84.12	7.01	82.0	6.83
N	0.96	0.07	1.83	0.13	0.8	0.057
O	1.2	0.075	2.63	0.16	7.2	0.45
S	4.7	0.147	1.02	0.032	0.9	0.03

Table 3 gives the ultimate analysis of a bituminous tar, a shale oil, and a coal tar produced in University of Utah laboratories. In processing each liquid hydrogen will be required to remove the nitrogen, oxygen and sulfur from the liquids in addition to that required to increase the hydrogen content of the hydrocarbon components.

Table 4. HYDROGENATION-DISTILLATION LIQUID  
FROM HIGH VOLATILE B BITUMINOUS COAL

Specific gravity, 20°C	0.9946°
Sulfur	0.3214 wt.%
Nitrogen	0.5820 wt.%
Tar acids	20.0 vol%
Distillation data	
I.B.P.	75°C
Up to 200°C	20.0 vol%
Up to 350°C	72.0 vol%
Hydrocarbon types in neutral oil	
Up to 350°C	
Saturates	46.0 vol%
Olefins	6.0 vol%
Aromatics	48.0 vol%

Table 4 gives a typical analysis of a liquid product from a partially hydrotreated coal distillate including the hydrocarbon type analysis in the liquid distilling below 350° centigrade. It is noted in this table that the bulk of the oxygen is present in tar acids which constitute 20% of the liquid distillate. Forty-eight percent of the

hydrocarbons in the neutral oil are aromatic.

The yield of liquid from coal or shale or tar sands depends very much upon the process used. This is also true of the quality of the distillate. Because of the different approaches to coal conversion, (1) straight carbonization pyrolysis, (2) hydrogenation-distillation and (3) solvent extractions, no single predictive method based on ASTM procedures is possible for determining the liquid product yield. For oil shale there has been developed the Fischer assay which gives the average yield of oil under a prescribed procedure of distillation<sup>(1)</sup>. In the Fischer assay, the oil yield is that amount of distillate which results from the pyrolysis of the higher molecular weight organic insoluble kerogen. Some hydrocarbons and other organic type compounds remain in the shale after the distillation. Methods which differ from the Fischer assay technique produce oils of very different quality and somewhat different quantity than the usual shale oil (1,2,3).

Due to the afore-mentioned instability of shale oil and oil from coal the second distillation in a processing scheme generally leaves a much greater carbon residue than is true with distillation of petroleum feed stock. Ultimate product yield therefore cannot be determined except by direct experimental measurement.

As the processed oils are up-graded, the data are reported according to the methods used in the petroleum industry. For example, pour point, viscosity and API gravity are regularly determined. It is important to bear in mind that the numerical value of these three properties will depend upon how quickly they are determined after the preparation of the initial liquid distillate.

#### ASSOCIATED MINERALS

The initial instability and the presence of nitrogen, oxygen, and sulfur compounds in larger amounts than in petroleum renders the hydrogenation treatment of the liquid more difficult than the comparable treatment of a petroleum oil fraction. Some work is now being carried out and much more must be done of the development of catalysts which will be as effective for shale oil and coal oil upgrading as are the catalysts currently being used in the petroleum industry. In particular is this true in terms of sensitivity to poisons present in the ash from coal or shale oil conversion. This becomes evident if we compare the ash content of the raw material feed stocks.

A petroleum crude contains negligible ash. The ash content of coal will range from 3 to 15 percent. The ash content of oil shale ranges from 85-92 percent, the ash content of in situ bituminous sand will range upward from 50 percent. Unfortunately many current methods of producing liquid petroleum supplement from coal, oil shale or tar sands carry over into the "hydrocarbon" stream as much as a few percent of the mineral matter associated with the raw material. The primary liquid therefore contains many times as much material which will interfere with the operation of a catalytic conversion process as does a petroleum fraction. It is therefore important for the potential refiner to know of this mineral matter content and its constitution. Different combinations of minerals are found in the

finest carried overhead in the oil shale pyrolysis and in coal pyrolysis. In addition to vanadium compounds there will frequently be significant quantities of nickel, iron, and other transition metal compounds. The problems presented by the different kinds of contaminants are in no way insurmountable but must be taken into account by potential processors of the supplemental feed stocks.

A possible plus in the area of mineral constituents is the catalytic activity possessed by some components. This has been noted particularly in the University of Utah laboratory in the high liquid yields from Assam India Coal subjected to hydrogenation-distillation with only the naturally occurring minerals present as catalysts.

The vanadium, nickel and iron contents of petroleum supplements from different coals differs markedly and should be studied more intensively to determine enhanced catalytic activity as well as catalyst poisoning effects.

#### VARIATIONS DUE TO PROCESSING

The basic quality of the liquids produced from fossil fuels other than petroleum varies tremendously depending upon the process followed. The Bureau of Mines has given valuable input data on several approaches and has carried out demonstration projects. The Office of Coal Research has supported several coal conversion projects through the pilot plant stage. Carbonization processes like the COED process of FMC Corporation recovers the smallest volume of hydrocarbon type liquids of the three types of processes currently under investigation.

Solvent extraction processes like those of Consolidation Coal and some petroleum companies give much higher liquid yields by extraction with hydrogen donor solvents. Intermediate in liquid product yield are pressurized distillation processes in a hydrogen atmosphere. The HRI process and the method developed at the University of Utah use this approach. The quality of the liquid varies markedly depending on the process used.

Accompanying the higher yield of the solvent extraction processes is an increase in the quantity of high molecular weight aromatic ring clusters in the liquid product. New catalysts must be developed to convert this portion of the liquid to gasoline range hydrocarbons in good yield. Otherwise, the bulk of this portion ends up as carbon residue.

Dr. G. Alex Mills of the Bureau of Mines has written an excellent review paper on the conversion of coal to gasoline<sup>(4)</sup> to which those interested in coal conversion processes and catalysts should refer.

Bituminous sand processing is very analogous in many regards to secondary recovery of heavy petroleum crudes. Various techniques are used to separate the bituminous material from the sand, clay and silt with which it is associated. The same possible processing difficulties encountered in processing shale oil and oil from coal will be anticipated unless a preliminary cleaning process is utilized.

That solid hydrocarbons can be converted into gasoline, diesel fuel and other salable products economically has been demonstrated during the past decade at the American Gilsonite Company oil refinery at Fruita, Colorado. The feed stock to this refinery has been the solid hydrocarbon, gilsonite, which is pipelined in a water slurry from Bonanza, Utah to Fruita, Colorado. After separation from the water the gilsonite is distilled in a primary coker. The liquid distillate is then hydrotreated and converted into the gasoline and diesel fuel used throughout the Grand Junction, Colorado market area. Problems of ash content in the feed stock and of the different metal compounds in the distillate have all been solved in the production of the gasoline which has been marketed at equal or lower cost than gasoline from conventional crude oils. There is no question about the ability of petroleum research, development, and production teams to utilize the supplemental feed stocks from other hydrocarbon sources as they become economic to use.

#### References

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