

BOTTOMS RECYCLE STUDIES IN THE EDS PROCESS DEVELOPMENT

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This paper will present the recent status of developments in moving the Exxon Donor Solvent coal liquefaction technology to commercial readiness. It will discuss results from the operations of totally integrated coal liquefaction pilot plants in which the vacuum tower bottoms are recycled back to the liquefaction reactor system. The paper will give an overview of the EDS coal liquefaction process and will present selected results of the vacuum bottoms recycle studies that have been undertaken to date. In discussing these studies, coal feed flexibility, yield and product flexibility and pilot unit operability will be stressed. Finally, these results will be summarized with a short discussion of the benefits and issues involved in EDS bottoms recycle development.

In the first figure options available with the EDS process involving liquefaction and bottoms processing technologies necessary to provide the required fuel and hydrogen are shown.

In the EDS process, coal is slurried with a hydrogen donor solvent. This slurry is fed in admixture with molecular hydrogen to the liquefaction system. The reaction products are separated by conventional fractionation steps into gases, liquids and a vacuum bottoms stream. Part of the liquid stream is catalytically hydrogenated in a fixed bed, hydrogenation reactor in the presence of molecular hydrogen and becomes the donor solvent. The hydrocarbon gas can be reformed to produce process hydrogen, it can be sold or it can be burned as a process fuel gas. Liquids are the ultimate product from the EDS process and are quality distillates boiling below 1000°F. Options for the vacuum bottoms include partial recycle, feed to a FLEXICOKING unit which produces liquids and process fuel gas or feed to a partial oxidation unit to produce hydrogen or fuel gas. For operations where the vacuum bottoms production is not sufficient to meet the necessary fuel and hydrogen requirements, additional coal can be used as feed to a partial oxidation unit to supplement hydrogen and fuel manufacture.

This paper will address results from the liquefaction step in the EDS process; or in Figure 1, the shaded portion. References will be made to bottoms processing for comparative purposes only.

In the development of the EDS process, extensive use has been made of small integrated coal liquefaction pilot plants of 75 pound-per-day and 1 ton-per-day feed coal capacities. The key features of these pilot plants are shown schematically in Figure 2. In the slurry preparation area, coal is slurried with a recycle donor solvent. The smaller unit uses a batch preparation technique involving manual addition of the solvent, crushed coal and bottoms (if recycled) on a six-hour frequency. The larger 1 ton-per-day unit has continuous slurry preparation. Both units feed from a slurry holding tank using high pressure positive displacement pumps.

The slurry is mixed with hydrogen before preheating and fed to tubular upflow reactors in both units. The reactors are staged to achieve the desired nominal residence time under study and the stages are connected by tubular transfer lines.

The liquefaction reactor effluent is separated by a series of conventional fractionation steps. Gases are separated by high and low pressure flashes. The unconverted coal and mineral matter are separated from the heavier coal liquids by recycle gas stripping in the smaller unit and by vacuum distillation in the 1 ton-per-day unit. Products are

split into naphtha and distillate using fractionation towers on both units. Part of the distillate is used for producing the recycle solvent.

This unhydrogenated distillate is introduced with molecular hydrogen into a conventional fixed-bed catalytic reactor. The hydrogenation conditions are tailored to produce the recycle solvent of the right specification, and this donor solvent is then used for slurring the crushed coal.

In Figure 3, one of the very important findings obtained early in the bottoms recycle studies is shown. These data show that coal conversion with vacuum bottoms recycle is very sensitive to the liquefaction conditions. In this figure, the pyridine insoluble fraction in the vacuum bottoms, on a DAF coal basis, is plotted against the hours of onstream pilot plant bottoms recycle operations. This data is for West Virginia coal (Ireland mine) and was obtained from operations using the 75 pound-per-day pilot unit. As was discussed above, the 75 pound-per-day pilot unit utilizes a batch slurry preparation technique. This is important because it influences the amount of time required for equilibration of the bottoms stream. This is evident from the very early period of time when the bottoms recycle mode of operations was just starting. During this period, the data show the pyridine insolubles are about 4-5% on a DAF coal basis. As time progresses, the pyridine insolubles are observed to be increasing with time. This is indicative of retrogradive reactions taking place in the liquefaction system and is a result of the necessary hydrogen not being available for quenching the reactive coal fragments. Consequently, the formation of pyridine insolubles increased to an equilibrated level of about 8% as the bottoms recycle operation was continued. In Figure 3, spot samples are shown as points, bars indicate periods during the operation used for material balance purposes. During this period of time there was no observed change in coal conversion over that observed from coal-only operations due to these retrogradive reactions taking place. After returning to coal-only operations in which the recycle of the bottoms was discontinued, the pyridine insolubles in the bottoms dropped back to their previous level of around 4-5%.

The data was initially puzzling but in fact helped in understanding the phenomena that were occurring. Earlier work had suggested the sensitivity of bottoms recycle to hydrogen availability. By increasing pressure and solvent-to-coal-to-bottoms ratio a continuation of the low pyridine insoluble content in the bottoms product was realized. This is also shown in Figure 3 and comes from the fact that additional hydrogen is being supplied from the gas phase as molecular hydrogen and from the liquid phase due to the higher level of donatable hydrogen present with the solvent. At the higher solvent rates and higher pressure that were employed in this successful bottoms recycle experiment, the coal conversion did increase. Discussion of the additional conversion from bottoms recycle will be presented in detail subsequently.

This study has been expanded from the West Virginia coal to include other coals including an Illinois No. 6 coal and the Wyoming coal. These data along with conventional coal-only data are shown in Figure 4.

In Figure 4, the 1000°F+ liquefaction conversion on a DAF coal basis obtained from the integrated pilot plants is presented. Here both the coal-only and bottoms recycle operations under EDS liquefaction conditions are shown. High conversions for all the coals in the range of 55-65% DAF coal are obtained with coal-only operations with the exception of the Illinois No. 6 Burning Star coal. These include bituminous, subbituminous and lignitic coals and confirm the fact the EDS process on a coal-only basis is applicable to a wide variety of coals. The initial data on the bottoms recycle operations show substantial increases in the conversion of the coal for three of the coals: the Illinois No. 6 and West Virginia bituminous coals and the Wyoming subbituminous coal.

In Figure 5, results are provided that show the liquid yields for the conversion conditions that were discussed previously. Despite the fact that there are differences in liquefaction liquid yields for each of the coals, additional liquids can be recovered from the FLEXICOKING operation on the bottoms to give total liquids of about 45-55% of DAF coal for all of the EDS program coals. For bottoms recycle, liquid yields of the same magnitude are achieved from the liquefaction step. Additional data will be forthcoming to define what additional liquids can be recovered from FLEXICOKING of vacuum bottoms from bottoms recycle operations.

In summary, pilot plant studies have successfully confirmed that the EDS process is flexible to process a wide variety of coals. In the 75 pound-per-day unit all of the EDS project coals have been processed to high yields of liquid products. In the 1 ton-per-day unit, investigation of three EDS project coals has confirmed the liquid yields from the smaller unit. Additional studies to investigate the remainder of the coals are planned using the 1 ton-per-day pilot plant.

Initial pilot plant studies indicate that bottoms recycle may be an attractive mode of operations. This is based on data from the 75 pound-per-day unit for three EDS project coals--the Illinois, the West Virginia, and the Wyoming coals and data from the 1 ton-per-day unit for the Illinois and Wyoming coals. Additional discussion of these data will follow.

The pilot unit data indicate there is a synerism between higher pressure and bottoms recycle which leads to the higher conversion and liquid yields. Small autoclave studies, although not covered here, indicate bottoms recycle is generally applicable under EDS conditions to all the coals discussed here.

In Figure 6, data showing the product distributions from bottoms recycle operations with Illinois No. 6 bituminous coal from the Monterey No. 1 mine is presented. The product yields in wt % based on the dry coal fed to the unit are shown for different operating conditions and for the different units. Comparison is made between a previous base set of coal-only operations which resulted in a liquid yield of approximately 34% on dry coal. These yields were achieved for coal-only conditions at 840°F, 60 minutes residence time, at 1500 pounds pressure. In the bottoms recycle mode of operation at 2000 psi an additional 7% liquids and an additional 10% C₁-C₃ gas is obtained. This is counterbalanced by increased hydrogen consumption of about 3 wt % on coal. These data have been taken from operations of the 75 pound-per-day unit and similar results are obtained from the operations of the 1 ton-per-day unit as shown in the companion figure. Here we do have a direct comparison at the higher pressure. Notice that the increase in liquids is maintained along with the increase in C₁-C₃ gas. As would be expected, the corresponding increase in hydrogen consumption is there also. In data from both pilot units, an increase in the amount of C₄-400°F naphtha is observed compared to coal-only operations.

In Figure 7, similar data are shown but for the Wyoming subbituminous coal from the Wyodak mine. The product yields for coal-only and bottoms recycle conditions from both the 75 pound-per-day unit and the 1 ton-per-day pilot unit are shown. Here the liquefaction conditions have been changed to 800°F, 100 minutes. From the 75 pound-per-day unit and for coal-only operations at 1500 psi approximately 29% liquids are obtained, for coal-only operations at 2500 pounds the liquids are increased to about 34%. For bottoms recycle at 2500 pounds an additional 7% liquids were recovered to total 42% based on dry coal. The increase in liquid yields is accompanied by a significant increase in the fraction in the C₄-400 naphtha and also in the C₁-C₃ gas. As would be expected these increases are accompanied by an increase in hydrogen consumption as was observed with the Illinois Monterey coal. The data from the 1 ton-per-day unit gives similar total liquid yields of around 43%. The product distribution is slightly different in that there is less of the C₄-400 naphtha and less of the C₁-C₃ gas. Here the comparison is data from 2000 pounds pressure operation with the data from 1500 pounds pressure operation for the Wyodak coal.

The results in Figure 8 are presented to show a wide range of flexibility with the bottoms recycle mode of operation to alter the product slate from essentially an all naphtha slate to one in which the naphtha content is approximately 50%. One set of data are from the 75 pound-per-day unit and one set from the 1 ton-per-day unit and it is expected that there will be slight differences in comparison but the general theme of the flexibility to change the product slate significantly is valid. Notice that the high liquid yields that were shown previously are maintained at the 42-44 wt % on a dry coal basis. The all naphtha product slate shows accompanying high C₁-C₃ gas yields. For the naphtha/fuel oil product slate, the naphtha is only about 50% and the 400-1000°F liquid is on the order of 50%. For the operating conditions leading to this product slate, the gas is substantially reduced.

In summary, the EDS bottoms recycle operations impact on the yield and product flexibility that can be obtained in the EDS process. Bottoms recycle operations provide increased liquid yields of about 8-10 wt % on dry coal and there is a general trend toward a lighter product slate. Bottoms recycle has provided product flexibility. Results showing an all-naphtha product and a naphtha/fuel oil product have been presented. Additional studies are currently underway aimed at a naphtha/distillate product. This would produce a product of all 700°F- material; part of which would be naphtha, part of which would be 400-700 distillate. The bottoms recycle mode of operations has been shown to be applicable to three coals--two bituminous coals and a subbituminous coal. As mentioned previously, based on small scale bench liquefaction studies, bottoms recycle should be applicable to all coals that are being investigated in the EDS project. This is an additional target of the current studies.

It is now appropriate to return to the discussion of the vacuum bottoms produced from coal-only and bottoms recycle operations. As discussed previously, in the initial studies of bottoms recycle operations for the West Virginia Pittsburgh seam coal, increases in pyridine insolubles due to retrograde reactions were occurring at conditions not optimum for bottoms recycle operations. The results shown in Figure 9 are for the Illinois No. 6 bituminous coal from both the 75 pound-per-day pilot unit and the 1 ton-per-day pilot plant. For all operations, the pyridine insolubles are approximately the same; in the range of about 16% of the 1000°F+ organics in the vacuum bottoms. The asphaltenes which are the benzene soluble fractions of the bottoms are on the order of 25-55% of the bottoms and the preasphaltenes are on the order of 55-25% of the bottoms. The use of bottoms recycle at the higher pressure significantly improves the quality of the bottoms as shown by the increase in asphaltene content of the bottoms when compared to the coal-only bottoms. This has led to better pilot plant operations and improved bottoms handling properties.

Additional data of this same nature is shown in Figure 10 for the Wyoming subbituminous coal. Here again comparison of data for both the 75 pound-per-day pilot unit and the 1 ton-per-day pilot plant is presented. For the 75 pound-per-day pilot unit, the data at 2500 psi show additional increases in the asphaltene content when bottoms recycle is compared to coal-only operations. In this figure, the pyridine insolubles for Wyodak bottoms are higher than for the Illinois bottoms and are approximately 20% of the DAF 1000°F+ bottoms. There is significant change in the asphaltene content based on the increased pressure; note that in the data from the 75 pound-per-day pilot unit, the asphaltenes increase from about 20% to about 43% for coal-only operations by increasing the pressure from 1500 psi to 2500 psi. Additional improvements in the bottoms quality is obtained by incorporating bottoms recycle into the operations. A similar relationship for the 1 ton-per-day unit is observed although the coal-only data at 2000 psi is not available.

In Figure 11, the results of the improved bottoms character is shown. The data in this figure show the vacuum tower bottoms viscosity in poise, measured at 550°F

and 21 reciprocal seconds shear rate as a function of the amount of liquids that are left in the vacuum tower bottoms. These liquids are characterized as nominally boiling in the 850-1200°F temperature range. Figure 11 shows two distinct sets of data: one for coal-only at 1500 pounds and one for bottoms recycle at 2000 pounds.

In Figure 11, data from two different pressure levels are being compared. The effect of higher pressure on coal-only data would be to move the coal-only curve directionally toward the bottoms recycle curve. Based on a small amount of additional data, these data sets are not expected to be identical. The data shown on this slide indicate that the conditions of the vacuum tower may be relaxed to give a similar amount of liquids in the bottoms for both coal-only and bottoms recycle but have a substantial decrease in bottoms viscosity for bottoms recycle.

In Figure 12, similar data for Wyoming subbituminous coal is shown. There is some overlap in the two data sets which was not observed with the Illinois coal operations. The viscosities for bottoms recycle derived bottoms are considered to be comparable or lower than those for coal-only derived bottoms. Here there is considerable scatter observed for the coal-only viscosities. This is contrasted to relatively tight band of data for bottoms recycle operations. This consistency of the bottoms recycle data compared to coal-only data on viscosities is indicative of the relatively uniform vacuum tower operation during bottoms recycle. The bottoms produced from bottoms recycle operations with Wyoming coal have essentially the same viscosity as the bottoms from the Monterey coal under coal-only conditions.

Alternative to operating the vacuum tower in a manner to deliver products with a single liquid content there is the opportunity to deliver bottoms at a specified viscosity. For this case, the bottoms from bottoms recycle operations will have less liquid associated with them compared to the bottoms from the coal-only operations. This would lead to additional liquid recovery for bottoms from bottoms recycle as opposed to the coal-only case.

In summarizing, operability advantages have been observed during bottoms recycle studies. Smoother pilot plant operations have been observed due in part, to higher asphaltene content of the bottoms which implies fewer degradative reactions. The vacuum tower operations have been more stable which probably follows from the lower bottoms viscosity and higher asphaltene content. Record operating times in both the 75 pound-per-day unit and the 1 ton-per-day unit have been achieved with bottoms recycle.

Overall, there are benefits from bottoms recycle operations but there are still concerns that must be addressed. Bottoms recycle operations result in higher conversions for three different coals. Bench scale laboratory studies imply general coal applicability of the bottoms recycle mode of operations, and the additional coals are under investigation. Product slate flexibility has been demonstrated and naphtha and naphtha/fuel oil product slates produced from operations of the integrated coal liquefaction pilot plants. Operating conditions for naphtha/distillate product slate are under investigation. Significant pilot plant operability benefits of longer, smoother operations due to the improved bottoms character have been observed. These benefits should translate into operability advantages for the larger 250 ton-per-day pilot plant.

Commercial application of EDS bottoms recycle will require reassessment of the process bases. The increased hydrogen consumption will require rebalancing of the hydrogen/fuel supply. The processability of higher ash containing streams will require further definition. Due to the additional recycle stream, higher investment and operating costs will result. Here the reduction in bottoms production implies only one bottoms processing technology would be necessary, but development of alternative bottoms processing technologies should be pursued to ensure flexibility and reliability. The lower bottoms production will also allow a decoupling of process fuel and hydrogen production which should improve startup, operability and the service factor of a commercial facility.

FIGURE 1

OPTIONS AVAILABLE WITH THE EDS PROCESS

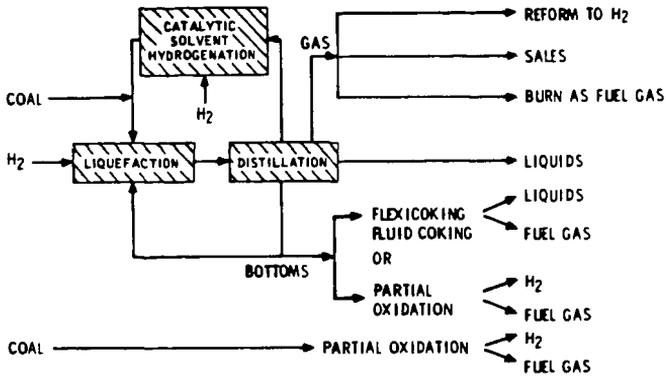


FIGURE 2

EDS COAL LIQUEFACTION PILOT PLANTS

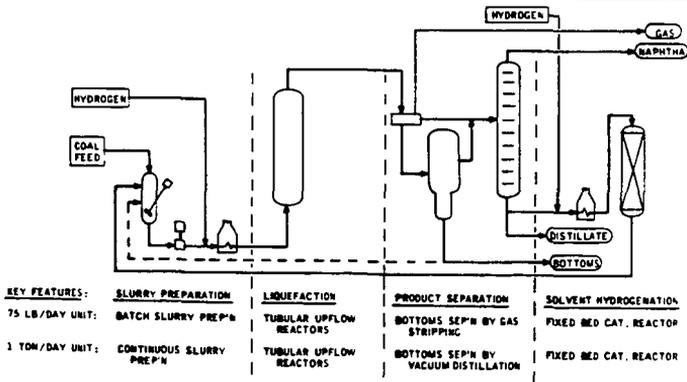


FIGURE 3
COAL CONVERSION SENSITIVE TO LIQUEFACTION CONDITIONS
WITH BOTTOMS RECYCLE OPERATIONS

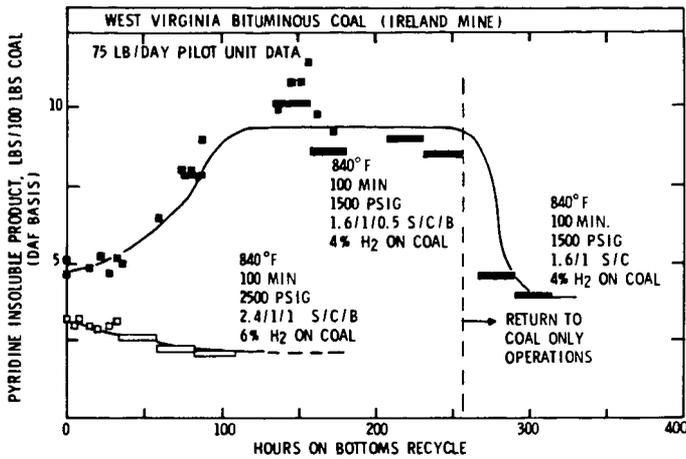


FIGURE 4
COAL RANK EFFECT ON CONVERSION

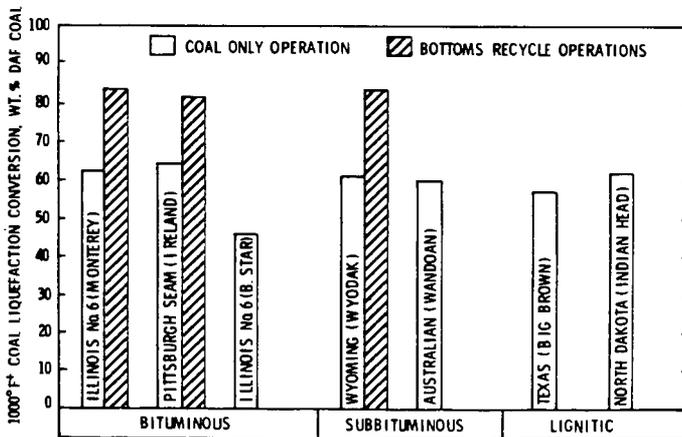


FIGURE 5
COAL RANK EFFECT ON LIQUID YIELDS

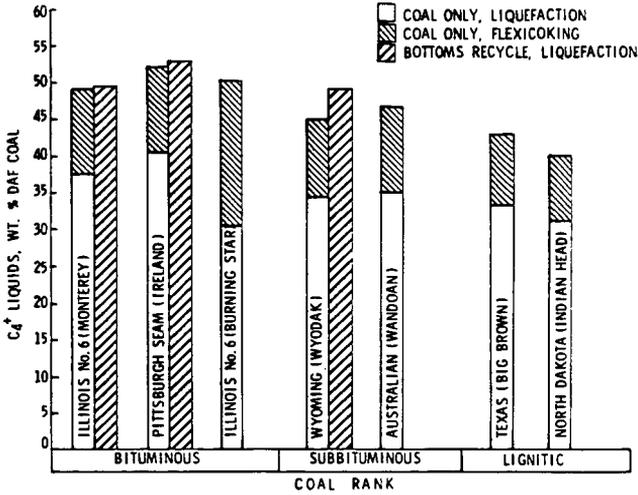


FIGURE 6
EDS BOTTOMS RECYCLE IMPROVES LIQUID YIELD
AND PRODUCES A LIGHTER PRODUCT SLATE

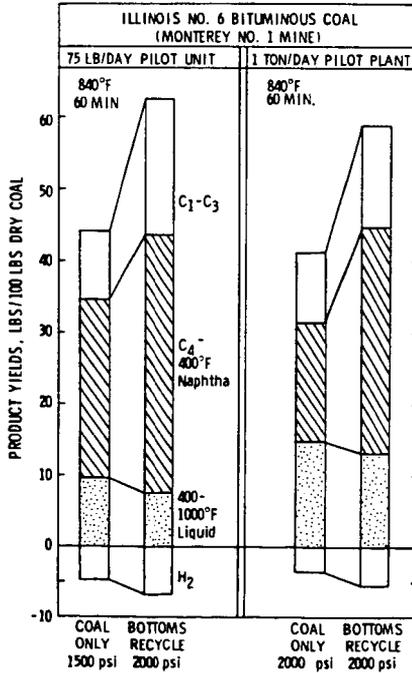


FIGURE 7

EDS BOTTOMS RECYCLE IMPROVES LIQUID YIELD AND PRODUCES A LIGHTER PRODUCT SLATE

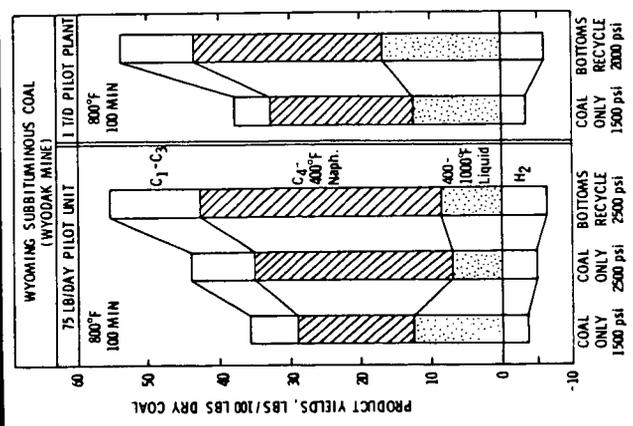


FIGURE 8

PRODUCT SLATE FLEXIBILITY ENHANCED WITH EDS BOTTOMS RECYCLE

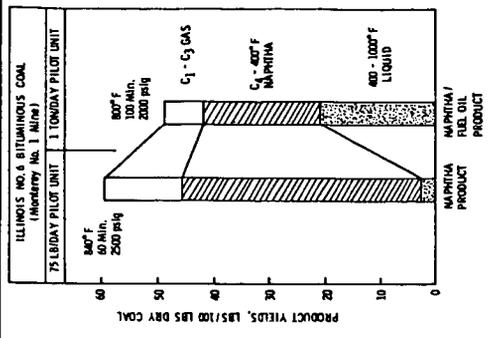


FIGURE 9

**BOTTOMS RECYCLE IMPROVES SOLUBILITY OF
BOTTOMS PRODUCT FROM BITUMINOUS COAL**

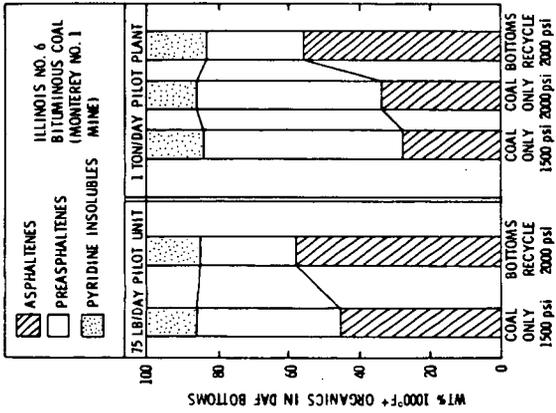


FIGURE 10

**BOTTOMS RECYCLE IMPROVES SOLUBILITY OF
BOTTOMS PRODUCT FROM SUBBITUMINOUS COAL**

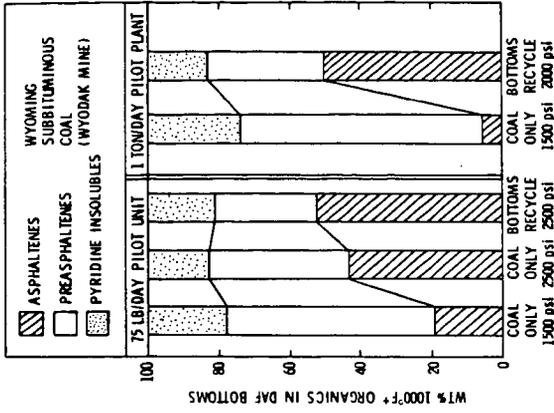


FIGURE 11

**EDS BOTTOMS RECYCLE WITH BITUMINOUS COAL
PRODUCES BOTTOMS PRODUCT WITH
LOWER VISCOSITY THAN COAL-ONLY BOTTOMS**

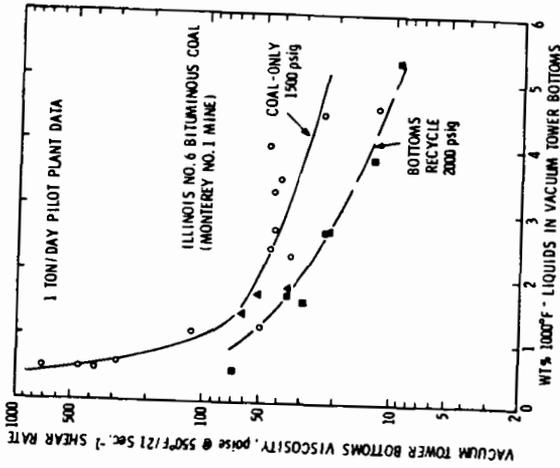


FIGURE 12

**EDS BOTTOMS RECYCLE WITH SUBBITUMINOUS COAL
SHOWS BOTTOMS VISCOSITY COMPARABLE
TO COAL-ONLY OPERATIONS**

