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Utilization of Tar from Low-Temperature Carbonization of Coal  
E. W. Lang and J. C. Lacey, Jr.  
Southern Research Institute  
Birmingham, Alabama

Recently-developed processes for fluidized low-temperature carbonization of coal promise to make available a large amount of low-cost tar in the near future. Because of the simplicity and relatively low cost of these processes, the power utility industry is seriously considering low-temperature carbonization as a means of reducing the cost of the solid fuels used. One large steam-generating plant could produce, through low-temperature carbonization of its coal, approximately 50,000,000 gallons of tar per year. The profitable disposition of the tar has been the major obstacle to commercialization of low-temperature carbonization of coal for several decades. The problem in finding outlets for the tar is difficult because it is quite different from coke-oven tar in physical and chemical properties and because the quantity that may be produced by several large steam-generating plants is so large. A fair amount of work has been or is now being carried out on determining the properties and composition of the tar (8, 10) and on developing uses for the tar (1, 2, 3, 4, 5, 6, 7, 9, 13, 14). But very little technical information is available from these programs. In the interests of making more information available, we wish to present the results from a preliminary program carried out in 1955 on the utilization of low-temperature tar.

This paper presents a summary of the work carried out at Southern Research Institute to evaluate the tar produced from Alabama bituminous coal and to investigate, in a preliminary manner, some methods for utilizing the tar. Also presented are the technical and economic aspects of two proposed means of processing the tar to salable products. The program was sponsored by the Alabama Power Company and its affiliate, Southern Services, Inc., in the interest of finding a means of reducing the cost of solid fuels.

Experimental Program on Utilization of Tar

This program on tar utilization was undertaken to provide a sounder basis for evaluating the potential of low-temperature carbonization for the sponsoring power utility. A prior program (11) for this power utility had demonstrated in a pilot plant that agglomerating coals could be carbonized economically in a fluidized-bed process. For a power plant application, the cost for carbonization and non-recoverable heat value of the original coal must be borne by the sale of the tar. Cost estimates indicated that carbonization would be economic if the tar could be sold for \$0.08 to \$0.10 per gallon. Disposal of the tar as a heavy liquid fuel would not always bring this required price. Therefore, for economic disposal of the tar, some premium values of the tar must be realized. Insufficient information was available in the literature on processing of low-temperature tar to marketable products to permit economic evaluation of proposed methods of processing. Also, the applicability of available data to the particular tar produced from

Alabama coals was not known. Therefore, an investigatory program was carried out (1) to evaluate in a preliminary manner various means of utilizing or converting the tar from the Alabama coals, (2) to determine approximate yields of salable products, (3) to reveal avenues of research that might be followed, and (4) to permit an approximate price tag to be put on the tar in terms of processing costs and prices of marketable products. The program was not intended to develop detailed and optimum procedures for each type of processing that was considered. Therefore, the results from this program are not precise, and the operating conditions and yields are probably not the optimum values that further research will provide.

### Tar Composition

Tar from the low-temperature carbonization processes is considerably different from high-temperature coke-oven tar. Low-temperature tar has undergone less thermal cracking and is, therefore, less aromatic in nature. It may be regarded as intermediate in nature between coke-oven tar and crude petroleum. Very few chemical compounds are present in sufficient amounts to permit their economical separation and recovery.

The tar used in this program was produced by carbonizing America Seam coal, a high-volatile bituminous coal from Alabama, at 950° F in a continuous fluidized-bed carbonization pilot plant (11). The tar is quite similar in physical and chemical properties to tars produced in other low-temperature carbonization processes from a variety of coals.

The composition of a typical tar used in these studies is shown in Table I. About 12% of the tar consists of low-boilers distilling below 235° C, 30% is middle oil boiling 235° to 360° C, and 58% is accounted for by the pitch and distillation loss. These yields are similar to those from coke-oven tar. The tar-acid content of the low-temperature tar (about 30% of distillate) is greater than that of high-temperature tar. The neutral oil from the distillate contains roughly 50% aromatic hydrocarbons, 40% saturated hydrocarbons, and 10% olefinic hydrocarbons. Table I also shows the composition of the low boilers (distillate to 235° C), the heavy distillate (boiling 235-360° C), and the distillate tar acids.

The pitch amounts to over 50% of the tar. It has a softening point of about 100° C after the distillables to 360° C have been removed. The pitch contains 4-10% char dust carried through the dust-collection equipment and 11-29% of the pitch is insoluble in benzene. Commercial dust collection equipment will keep the dust content of the pitch from a large plant at a lower level.

### Light Distillate

The light distillate fraction boiling below 235° C has a much greater value than the other fractions because approximately 30% of it consists of phenol, cresols, and cresylic acid. Aromatics (40% of the remaining neutral oil) can be recovered, but the oil would be more valuable if the aromatic content of the oil were increased. Therefore, two runs were made in a continuous bench-scale pressure reactor using reforming conditions to study the possibility of converting the naphthenes in the light distillate to aromatics.

The reactions were carried out in a bench-scale continuous reactor containing 550 ml of 1/8-in. standard molybdena-alumina catalyst. The conditions of the runs included a space velocity of 0.4, a catalyst temperature of 525° C, and a flow of hydrogen at 370 psig.

In two runs made with neutral oils from the light distillate, the aromatics content of the oil was increased from 38% to 65% at a yield of 71 vol-%. Nitrogen and sulfur compounds were practically eliminated under these conditions.

#### Heavy Distillate

To study the possibility of converting the heavy distillate to more valuable low-boiling compounds, the fraction of the tar boiling between 235° C and 360° C, including the tar acids, was treated by catalytic means in both batchwise and continuous runs.

The four batchwise hydrogenation runs were made with maximum hydrogen pressures of 3000 to 4000 psig, temperatures of 450° C to 500° C, and a molybdena-alumina catalyst. After a reaction time of 1.5 hr, the yield of oil was 93 vol-%; 45% of the product boiled below 235° C, and the product contained 55% aromatics. The consumption of hydrogen was 5.5% of the weight of the tar. These runs indicated that 475° C was about the optimum temperature, and that the yields were much lower with longer holding times and at higher temperatures.

The continuous runs were made in a bench-scale unit which had a reactor catalyst volume of 550 ml. They were made at a temperature of 480° C, a hydrogen pressure of 3000 psig, and a space velocity of 0.4 to 0.8. The catalyst was 1/8-in. pellets of molybdena alumina. Under these conditions, very little of the aromatic compounds was hydrogenated and the desired degree of cracking to the low-boiling compounds was accomplished. The tar acids were practically eliminated under these conditions. The results from the continuous runs were quite similar to those from the batchwise runs. On the basis of five runs, the best yields at these conditions were approximately 92 vol-% and the amount of the product boiling below 235° C was 50%. The product contained 40% aromatics.

The hydrocracked oils boiling below 235° C still contained considerable amounts of naphthenes and their conversion to aromatics via reforming was studied in a single continuous run. The equipment and conditions were the same as used for reforming of the low-boilers distilled from the tar. An oil yield of 74 vol-% was obtained. The product contained 80% aromatics as compared to 44% aromatics in the charge stock. A more complete study of reforming of hydrogenated or hydrocracked oils from tar should demonstrate higher yields.

#### Neutral Heavy Distillate

It is probable that in commercial processing of the distillate oils, the tar acids will be extracted for separate processing before the oils are catalytically treated because such treatments destroy the tar acids. A number of continuous runs was made with this neutral heavy distillate to determine the effect of thermal cracking at atmospheric pressure with and without catalyst and the effect of a low-pressure reforming-cracking reaction. The neutral heavy distillate used for these runs was the fraction of the total tar boiling from 235° C to 360° C after the tar

acids were extracted with caustic washing. Under the best conditions, the heavy oil was cracked in a single pass to products of which 40% boiled below 235° C and which had high aromatic contents of 75% to 80% at a yield of 75 vol-%.

Thermal cracking runs on the neutral distillate made without a catalyst at 600° C and at atmospheric pressure resulted in yields of approximately 80 vol-%. Only about 17% of the product boiled below 235° C. Another series of runs was made using molybdenum sulfide-alumina catalyst and hydrogen at atmospheric pressure at a space velocity of 1.0. At a temperature of 640° C, the yield was 55%, and the product contained 77% aromatics and 22% of oils boiling below 235° C. At a lower catalyst temperature of 520° C, the yield was 87%, but the product contained only 16% of oils boiling below 235° C. These runs indicated that satisfactory yields of cracked products can be obtained only when a catalyst and sufficient hydrogen pressures are used to prevent cracking from proceeding too far.

A series of runs on the neutral heavy distillate was then made using hydrocracking-reforming conditions of 500 to 750 psig hydrogen pressure and temperatures of 480 to 550° C. The previous runs with total heavy distillate showed that fair yields of aromatics boiling below 235° C could be obtained by first hydrocracking the oils to low-boiling oils and then reforming the low-boilers to aromatics. This present series was made under conditions that combined those of the previous two-step treatment. A fairly high temperature was selected to give sufficient cracking and dehydrogenation and a moderate hydrogen pressure was selected to prevent over-cracking of the compounds so that good liquid yields would be obtained. The selection of these conditions was based partially upon a series of batch reactions with heavy distillate.

With the use of a molybdena-alumina catalyst at about 480° C, a hydrogen pressure of 750 psig, and a space velocity of 1.0, yields were 75-91 vol-%. The product contained 73-80% aromatics and 40% boiled below 235° C. With a temperature of 550° C, hydrogen pressure of 500 psig, and a space velocity of 0.4, the yield was 74 vol-%, the product contained 79% aromatics, and 46% of the product boiled below 235° C. In a commercial operation, the oils boiling above 235° C would probably be recycled to the reaction so that only low-boilers would be produced. One run was made to determine the effect of recycling the high-boiling oil. The yield of product was 66 vol-%. The product contained 93% aromatics and 26% boiled below 235° C.

The combined reformat boiling below 235° C from the primary run and the recycle runs was carefully fractionated and the aromatics in each fraction determined. This analysis indicated that the combined chemical oil contained 4% benzene, 8% toluene, 10% xylenes, 16% naphthalene, 30% substituted benzenes, and 32% saturated hydrocarbons.

#### Tar Acids

As shown by the typical analysis in Table I, approximately 40% of the tar acids from the total distillate consists of phenol, cresols, and xylenols. About 60% consists of high-boiling, highly-substituted alkyl phenols for which there is little demand at the present. The research program has shown that the tar-acid fraction boiling from 170 to 235° C (including xylenols) will form hard thermosetting resins with formaldehyde. The removal of small amounts of impurities

from individual tar acids appears to be a major problem.

One means of utilizing the tar acids is to convert the higher-boiling ones which have little value to the simpler, more valuable low-boiling phenolics. The hydrocracking of these high-boiling tar acids was studied in five batchwise runs with a molybdena-alumina catalyst in the presence of water. Tar acids boiling from 235 to 360° C were hydrocracked at a temperature of 420° C, in the presence of 10% addition of water, and a hydrogen pressure of 2600 psig. The yield was 92 vol-%. The product contained 82% tar acids and 23% oils boiling below 235° C. The tar acids boiling in the intermediate range of 235 to 300° C were hydrocracked at 460° C and 2100 psig hydrogen pressure to give a yield of 90 vol-%. The product contained 50% tar acids and 53% boiled below 235° C. Hydrocracking of the heavy tar acids boiling at 300-360° C resulted in a yield of 84 vol-%. The product contained 50% tar acids, and only 23% of the product boiled below 235° C. Additional runs with this fraction were made in which nitrogen replaced some of the hydrogen in an attempt to limit the hydrogenation of the hydroxyl groups and yet provide sufficient pressure to suppress the cracking to gases. These runs gave rather low yields of oils and a large amount of coking.

#### Pitch

Approximately one half of the tar consists of hard pitch. Therefore, no plan for conversion of the tar will be successful unless attractive markets or methods of conversion for the pitch are found. The pitch might be sold in the large-volume markets of road asphalt or pitch, roofing pitch, electrode binder pitch, or for a premium fuel in open-hearth furnaces of steel mills. The pitch might also be converted to pitch coke or hydrogenated to give more of the low-boiling chemical oil. Preliminary investigations were made for adapting the pitch to these various outlets. Additional work on making the pitch more stable to weather is needed if it is considered for uses such as road and roofing pitch.

Experiments showed that the specifications for highway road-tar primer could be met by blending high-boiling neutral oil with pitch. However, this method would use up more of the heavy distillate than pitch and would degrade the value of the distillate used to road-tar price.

Electrode binder pitch must contain at least 20% of so-called "beta resin" which is that portion soluble in quinoline, but insoluble in benzene. Normally, low-temperature tar pitch has a very small amount of this beta resin. A series of experiments demonstrated that the beta-resin content of the pitch could be increased to the range of 30 to 50% in yields greater than 95% by air-blowing at 250° C. No catalyst was used in any of the runs. This air-blown pitch meets most specifications for electrode binder pitch, but its utility for this purpose needs to be tested.

Coking of the pitch was studied in five batchwise retort runs made at 700° C. The average yield of coke was 51% and that of tar was 31%, with the remainder being water and gas. The coke had a volatile content of 5%. The pitch used for these tests had a high content of char dust which caused a high ash content in the coke. The tar from the coking of pitch was very viscous and contained only 19% of oils distillable to 360° C.

## Tar Hydrogenation

A limited number of batch hydrogenations was carried out using the total tar which had been topped to 235° C. Such hydrogenation of the total heavy tar might be considered for commercial utilization of the tar if previously mentioned uses of the tar do not provide sufficiently attractive outlets. Low-temperature tar is much more reactive than coke-oven tar, and has been hydrogenated to low-boilers in yields of approximately 100 vol-% in other research programs. The two runs made in the present program were carried out at temperatures of 450 and 470° C, and at maximum hydrogen pressures of about 3000 psig. Yields of 90 and 98 vol-% were obtained, and 20 to 30% of the product boiled below 235° C. The conversion to low boilers was not as great as desired, and further study is needed.

### Possible Methods for Processing the Tar to Marketable Products

A large number of means for utilizing the tar are potentially available—from crude uses such as for fuel and road tars to complete conversion to low-boiling aromatics. The optimum combination of processing methods will be determined through future research, by existing and future markets, and by the economics of such combinations of processing methods.

Several schemes for partial or total conversion of the tar to marketable products were considered on the basis of the results from the preliminary experimental program and on published data. Two possible methods of processing the tar are presented to illustrate what might be done, and to indicate the approximate economic potentials of such processing plans. The estimates were based on a plant processing 41,600,000 gallons of tar per year produced by fluidized carbonization of 6,000 tons of America Seam coal per day. The costs of equipment and processing were obtained from published data on plants carrying out these or similar steps. Since the cost data used were averages of as many as 20 to 30 reported costs, it is believed the data are representative of the cost of an average processing step. In each case, conservative (higher-cost) figures were used. The tar was charged to the tar processing plant at \$0.086/gal because a cost study indicated that such a price would give a net return of 10% after income taxes on a carbonization plant located in Alabama. These costs were based, in part, on an engineering cost study of fluidized carbonization by United Engineers and Constructors, Inc. (12).

The first of the two proposed plans for tar processing involved using a portion of the tar without chemical conversion and converting the remainder by hydrocracking. The low-boiling oils are removed and refined to tar acids and a neutral oil. The pitch and nonaromatics from the heavy distillate are sold as road binder. The aromatic portion of the heavy distillate is hydrocracked to low-boiling oils. The refined products consist of low-boiling aromatics, cresylic acid, and gasoline blending stock.

The total plant cost was estimated to be \$6,470,000, of which \$2,628,000 was for the hydrocracking unit. After including \$1,310,000 for working capital, the total capital requirements were \$7,780,000. The processing costs included amortization, direct and indirect production costs, raw material (tar) costs, and sales and administrative costs. The estimated net income after income taxes was

\$979,000, which gives a net yearly return on the investment of 12.6%, or a payout time of 4 years.

The second plan was for the complete conversion to low-boiling products. This plan was proposed for the eventuality that the pitch and heavy distillate cannot be sold in existing markets or would bring only fuel prices.

This method of utilization calls for removing the tar acids boiling below 300° C, and hydrocracking the rest of the tar to oils boiling below 235° C. The heavy tar acids are also hydrocracked to cresylic-acid range or below. The final products consist of refined tar acids, refined aromatics, and a gasoline blending stock. The over-all yield of finished products was 68 gallons per 100 gallons of crude tar.

The estimated cost of the plant was \$13,152,000, including working capital. The total yearly costs for processing the tar were estimated at \$3,733,000. The net income after income taxes for this plan is \$912,000, which provides a return on the investment of 6.9%.

#### Present Outlook

The return on the investment for either of these plans is lower than that expected by most chemical companies for processes that will involve heavy expenses for development work. There are several factors that may improve the economics of processing low-temperature tar: (1) further research may result in higher yields of the valuable products from the tar; (2) further research and advancing technology are expected to reduce the complexity and the costs of processing the tar; (3) long-term increases in costs of competitive raw materials and of finished products will better the economics of tar processing; (4) further development work on the carbonization process should result in increased yields of tar from the coal and lower costs of carbonization.

Counterbalancing these optimistic factors are some dampening factors that have become apparent since the fall of 1957. The general recession in 1958 caused softening of prices of the aromatic chemicals and of certain fuel fractions for which some of the tar would be used. It may be several years before these losses may be overcome by rising prices. The increasingly large amount of imported petroleum of the past few years has softened the price of fuels and petroleum products with which some of the tar products must compete.

It now appears that the conversion of tar into chemical products on a commercial scale is a matter of 5 to 10 years in the future. When petroleum and residual fuel prices increase to approximately \$0.10/gal at inland coal-producing areas, operation of commercial carbonization plants should be profitable through the sale of tar as a liquid fuel. Once low-temperature carbonization is on its feet through sale of tar as fuel, then commercial processing of the tar to chemicals and higher-priced products will follow.

Table I. Properties of Typical Tar from America Seam Coal

Specific gravity 25/25° C, 1.10

Distillation yields, weight % (Hempel)

to 170° C	1.4
170-200	3.3
200-235	7.6
235-270	7.3
270-300	7.5
300-360	14.3
pitch	51.8
loss	6.8

Composition of distillate, volume %

tar acids	28.5
tar bases	2.9
neutral oil	68.6

Composition of distillate tar acids

<u>Fraction</u>	<u>Major Component</u>	<u>Weight %</u>
170-200° C	phenol	3.1
200-210	cresols	13.9
210-235	xlenols	22.0
235-300		20.8
above 300 and loss		40.2

Composition of distillate neutral oil, volume %

Olefins	8.1%
Aromatics	47.3
Saturated hydrocarbons	44.6

Composition of low boilers (to 235° C), volume %

Tar acids	28.5
Tar bases	2.2
Neutral oils	69.3
Olefins	11.2
Aromatics	33.2
Saturated hydrocarbons	50.6
Naphthenes	41
Paraffins	59

Composition of heavy distillate (235-360° C)

<u>Distillation range</u>	<u>Weight %</u>
to 235° C	6
235-270	14
270-360	48
Residue	32

Composition, - volume %

Tar acids	35.7
Tar bases	3.4
Neutral oil	61.0
Aromatics	51.6
Olefins	19.2
Sat'd hydrocarbons	29.2

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