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PRODUCTION OF HIGH QUALITY LUMP
COKE FROM LIGNITIC COALS

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This invention relates to a process for produc-
ing a strong, coherent, porous lump coke of good
quality from a low ranking, normally non-coking
coal. The invention also relates to the resultant
product. More particularly, the process involves
carrying out a Pott-Broche type solvent extrac-
tion on a normally non-coking coal of the lignitic
class, such as lignite, followed by recovery of the
solvent and coking of extract-residue mixture.

Heretofore, it has been considered possible to
produce a strong, coherent, agglomerated coke,
such as that required for metallurgical and other
commercial purposes, only from the so-called
"coking coals." A coal is said to be of the "cok-
ing" or "caking" variety, if, when heated in the
absence of air, the coal softens and eventually
solidifies to form a solid cake. If the final prod-
uct is granular or weakly coherent and crum-
bles easily, the coal is classed as non-coking.
Caking and coking properties are confined en-
tirely to coals of bituminous rank; see "Encyclo-
pedia of Chemical Technology," by Kirk and
Othmer, Interscience Encyclopedia, Inc., New
York, 1949, vol. 4, page 130. Lignitic coals, i. e.,
lignite and brown coal, are of lower rank than bi-
tuminous and are classed as non-coking coals.
It is to these low ranking coals that this inven-
tion pertains.

Attempts have been made to produce good
quality lump coke directly from the low ranking,
non-coking coals mentioned above. Such results
are desirable because of the abundance and low
cost of these low grade starting materials. Such
attempts, however, have resulted in failure, the
products being only weakly consolidated or com-
prising a powdery substance having no coke
structure.

It has also been attempted to treat these low
grade coals in such a manner as to improve their
coking characteristics. For example, it has been
suggested by Alfred Pott and Hans Broche, the
originators of the Pott-Broche process to per-
form an extraction on low grade solid carbona-
ceous fuel with an organic solvent at elevated
temperature. According to this process, the res-
idue is removed by filtration or centrifuging, and
the resulting extract is then destructively distilled
to a solid residue. Although the residue obtained
by this procedure is relatively ash-free carbona-
ceous material, it is granular or powdery and
easily friable, having a poor coke structure. Res-
idues produced in this manner accordingly have
found use only in the manufacture of electrodes.

It is a principal object of this invention to pro-
duce a strong, coherent, porous, agglomerated

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commercial coke of good quality from the non-
coking lignitic coals. A further object is to pro-
duce, in addition to good quality lump coke, val-
uable liquid products boiling in the gasoline and
fuel oil ranges. A further object is to produce
useful liquid and solid products with the elimina-
tion of the normally employed, difficult filtration
of the tarry extract-residue mixture. Other ob-
jects will appear hereinafter.

These and other objects are accomplished by
my invention which comprises extracting a lig-
nitic coal in the presence of hydrogen available
at extraction conditions with a solvent from the
group consisting of polynuclear aromatic hydro-
carbons, hydrogenated polynuclear aromatic hy-
drocarbons, and their mixtures with a phenolic
compound, at elevated temperature and, where
necessary, at superatmospheric pressure at least
sufficient to retain reactants and products. Sol-
vent is recovered from the resulting solvent-ex-
tract-residue mixture, and the extract-residue
mixture is destructively distilled to remove vola-
tile matter. The invention also includes the
product resulting from the process.

While certain preferred embodiments of the
invention are set forth in the accompanying
specification, it is understood that they are by
way of illustration only and are not to be con-
sidered as limiting.

In general, the first step of the process involves
carrying out a Pott-Broche type solvent extrac-
tion on a non-coking coal of the lignitic class,
such as for example, lignite. This procedure
usually includes heating the lignite charge in a
closed vessel with an organic solvent. For the
purposes of this invention the extraction must
be carried out in the presence of hydrogen which
is available at extraction conditions, by which is
meant either gaseous hydrogen or hydrogen dis-
associated from a constituent of the solvent. Nu-
merous variations of the Pott-Broche extraction
process are known, which variations are applica-
ble to the procedure described above. Thus the
reaction may be carried out, for example, in the
presence of added hydrogen, and under addi-
tional pressure. In certain modifications of the
extraction step the presence of a hydrogenation
catalyst may be desired. These and other varia-
tions will be discussed more fully hereinafter.

Upon completion of the extraction, the entire
solvent-extract-residue mixture is treated to re-
cover solvent, e. g., by distillation. This may be
accomplished by separately distilling off solvent
from the entire mixture, as is preferred, or al-
ternatively, by transferring the solvent-extract-

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residue mixture intact from the extraction vessel to the coking retort. In the latter instance, the solvent is distilled off with volatile coking products from which it subsequently may be recovered by distillation. In either instance, the coking retort contains a mixture including predominantly the extract-residue mixture at some time.

This mixture of extract and residue is destructively distilled or coked by heating in the absence of air to drive off volatile matter. The coke remains as residue in the distilling or coking vessel and is recovered as such. Liquid products distilled off during the coking step are also recovered. These products may be further processed in known manner to improve the quality thereof, or alternatively, they merely may be fractionated into cuts useful as such without further treatment.

The coking or destructive distillation of the tarry extract-residue mixture brings about the formation and/or removal of certain volatile materials from the distilland. This may be accompanied by swelling and foaming of the viscous material to be coked. In many cases the foaming is so extreme as to cause substantial portions of the distilland to pass out of the retort and into the receiving vessel. Accordingly, an advantageous modification of the invention involves the taking of measures to suppress the foaming mentioned above.

One such measure may include coking of the extract-residue mixture in admixture with an effective, foam inhibiting amount of a polymeric organo-silicon oxide compound. These compounds are known more commonly as silicones and are effective in extremely small amounts to inhibit the foaming characteristics of the distilland.

Additional advantages in this respect may be obtained by applying all or at least a major amount of the heat to the top and sides only of the distillation or coking vessel over the temperature ranges during which the greatest evolution of volatile material and the greatest tendency toward foaming occur. Radiant heat from the inner surfaces of the vessel is thereby applied to the distilland from above. This procedure not only aids in reducing or preventing foaming of the distilland, but is of additional value in that it prevents condensation of vapors on the upper surfaces of the coking vessel. Consequently tarring and coking of the take-off lines is prevented.

The use of the silicone anti-foam agent together with the described controlled heating steps constitutes a preferred technique in carrying out the destructive distillation steps, since what otherwise may be an extremely difficult procedure is greatly simplified.

As an illustration of the benefits to be obtained from my invention, the following specific example is presented:

Example 1

One hundred parts of lignite and 200 parts by weight of a 4:1 mixture of tetralin and cresol were placed in a rocking autoclave, and gaseous hydrogen was added to a pressure of 1000 p. s. i. g. The autoclave was then sealed, heated to 824 degrees F., maintained at that temperature for 45 minutes, and then cooled. The autoclave was rocked during the entire cycle to insure thorough mixing of the contents. After the gas had been vented off, the autoclave was opened and the entire contents of the vessel were transferred to a

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glass retort. About 0.03% of Dow Corning Silicone Fluid 200 was added to aid in reducing foam formed in the coking operation. The retort was heated by a flame directed against the bottom until the temperature of the charge reached about 500 degrees F., at which point most of the solvent had been distilled off. The bottom heating was then discontinued and heat was applied to the top and sides of the vessel until the temperature of the charge reached about 930 degrees F. Heating of the sides, top, and bottom of the retort was then continued until the temperature reached about 1110 degrees F., at which time no further evolution of gases or liquids could be observed. Yields traceable to the lignite charge were obtained from the combined operations as tabulated below:

	Yield, weight per cent of dry lignite charged
20 Gas plus loss	20.2
Liquid product (inc. tar)	45.9
Coke	33.9

Fractionation of the liquid product gave the following over-all yield distribution:

	Yield, weight per cent of dry lignite charged
25 Gas	13.5
Water	11.1
30 Hydrocarbon boiling below 428 degrees F. ¹	11.4
Hydrocarbon boiling between 428 deg. and 563 deg. F.	4.5
Products boiling above 563 deg. F.	15.1
Coke	33.9
35 Loss (inc. distillation loss)	10.5
	100.0

The coke from the experiment was removed from the retort and examined. It was found to be a hard, coherent mass full of uniformly small pores. In hardness and density it closely resembled the highly useful cokes made from "coking coals."

A further example of this invention is as follows:

Example 2

In this experiment 100 parts of lignite and 133 parts by weight of the same solvent were reacted as described in Example 1. The entire reaction mixture, except for gas formed, was carbonized, after recovery of solvent, under substantially identically the conditions described in Example 1. The following total yields, based on dry lignite charged, were obtained:

	Weight Percent
55 Gas plus loss	17.1
Tar plus light oil	45.1
Coke	37.8

The coke obtained from the experiment equalled or surpassed the product of Example 1 in the qualities mentioned.

Additional experiments were carried out to determine the individual coking properties of the extract and residue. The results of these experiments are presented in Example 3:

Example 3

100 parts of lignite were treated with 200 parts of 4:1 tetralin-cresol mixture and hydrogen at 824 deg. F. for 45 minutes as in Example 1. The contents of the vessel were filtered and

¹The weight of the tetralin-cresol charged was subtracted from this fraction in calculating the yields on a dry lignite basis.

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thus separated into an "extract solution" containing 53.4% of the lignite in solution, and into an undissolved residue. The extract solution was distilled to dryness as in Example 1. The yield of products from this experiment was:

	Yield, weight per cent of dry lignite charged
Gas plus loss.....	15.9
Tar plus light oil.....	46.0
Solid residue.....	38.2

The residue was removed from the apparatus and examined. It was found to be a voluminous, fluffy, friable mass similar to residues obtained from the charring of sugar, etc. When the undissolved residue from the extraction was heated to 1112 deg. F., it produced a small amount of gas and tar; most of it remained as a powdery char with no coke structure.

The following example is illustrative of the results obtained by direct coking of lignite:

Example 4

One hundred grams of dry lignite was carbonized in the apparatus of Example 1. The yields from this experiment were:

	Yield, weight per cent (based on dry lignite charged)
Gas plus loss.....	28.1
Tar plus light oil.....	7.1
Char.....	64.8

The char from this experiment was a powdery, soft product with no coke structure.

A comparison of the results of Examples 1 or 2 and 4 indicate the improvements effected by my invention. An examination of the results obtained in Example 3 indicates that the beneficial results obtained by the invention are dependent upon the presence of both extract and residue. Summarizing, these results show that carbonization of the lignite alone, or of the filtered extract obtained therefrom, or of the residue from such filtration, produces only a powdery char, while the subject process yields a dense coke in lump form.

My invention is applicable to coals of the lignitic class which includes lignite and brown coal.

As stated previously, the preliminary extraction is of the Pott-Broche type. By this is meant that the extraction is carried out with an organic solvent, e. g., tetralin, or a mixture thereof with a phenol, at temperatures sufficient to effect substantial decomposition. Satisfactory temperatures are between about 480° F. and about 900° F. and preferably between about 750° F. and about 860° F. However, the invention is not limited to these temperatures. While the temperature ranges mentioned are desirable from the standpoint of producing good liquid product yields in addition to good quality coke, somewhat lower or higher temperatures produce satisfactory results.

Normally, the extraction is carried out in a closed vessel at least at autogenous pressure. The use of a closed vessel permits the retention of solvent and reaction products at the temperature of extraction. When certain high boiling solvents are employed, e. g., a hydrogenated chrysene, the extraction may be performed at the boiling point of the solvent and at atmospheric pressure under reflux without loss of solvent. Such an extraction has been successfully performed with a hydrogenated chrysene (B. P. 705° F.).

Solvents which may be satisfactorily employed

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are certain of those which are commonly utilized in the Pott-Broche process. Examples of these are polynuclear aromatic hydrocarbons, as naphthalene, phenanthrene, anthracene, and chrysene, their hydrogenated products, such as tetralin (tetrahydronaphthalene), decalin, etc., or one or more of the foregoing in admixture with a phenolic compound such as phenol or cresol. These solvents need not be pure and may be used in the presence of other materials. For this reason, fractions of the liquid product obtained from the coking step of this invention and containing certain of the foregoing satisfactory solvents may be employed either alone or to supplement the starting materials. Tetralincresol is a preferred solvent mixture because of superior results produced. Hydrogenated chrysene is another preferred solvent, since it eliminates the need for extracting the coal under pressure. When employing a mixture of solvents, such as, for example, tetralin-cresol, any ratio of solvents may be employed, so long as the polynuclear aromatic component is present in substantial proportions. It is preferred however to employ a ratio in which the proportion of the polynuclear aromatic component equals or exceeds the proportion of the phenolic component. Examples of the operative polynuclear aromatic compound: phenolic compound ratios are those between about 1:2 and 10:1. Examples of preferred ratios are between about 1:1 and 5:1. The solvent or solvent mixture may be added to the coal in a ratio between about 1:2 and 2:1. Higher ratios may be employed, but with little or no further advantages.

As mentioned previously, for the purposes of this invention the extraction must be carried out in the presence of hydrogen available at extraction conditions. This hydrogen may be provided in the form of gaseous hydrogen added before or during the extraction, or it may come from the dehydrogenation of a hydrogenated polynuclear aromatic solvent. The hydrogen available at extraction conditions may also come from a combination of the above-mentioned sources. Thus, satisfactory conditions for the invention are produced by the use of a polynuclear aromatic compound in conjunction with gaseous hydrogen, and by the use of a hydrogenated polynuclear aromatic compound with or without added hydrogen. A phenol may be employed in conjunction with any of the above.

The hydrogen atoms which distinguish a hydrogenated polynuclear aromatic compound from the parent polynuclear aromatic compound are rather loosely associated in the molecule and are released at the conditions of the extraction. Thus, tetralin is dehydrogenated to naphthalene during the extraction. For this reason where the available hydrogen is supplied only by the partial dehydrogenation of the hydrogenated polynuclear aromatic compound, it is necessary to rehydrogenate the resulting polynuclear aromatic compound prior to its reuse in the extraction phase. This may be accomplished in conventional manner, e. g., hydrogenation with gaseous hydrogen under pressure and in the presence of a conventional hydrogenation catalyst.

Where gaseous hydrogen is added to the extraction vessel, rehydrogenation of the solvent is unnecessary.

The preliminary extraction is carried out under a pressure sufficient to retain the gaseous hydrogen, if used, the solvent, and other volatile materials present in or formed from the solid carbonaceous charge. The elevated pressure

may conveniently be the autogenous vapor pressure and may be maintained simply by performing the extraction in a closed vessel. If desired, however, the extraction step may be performed in the presence of added hydrogen and at greater pressures, e. g., from about one hundred to one thousand p. s. i. g., or much more. Hydrogenating catalysts, e. g., molybdenum oxide or sulfide, iron, nickel, chromium oxide or sulfide, tungsten oxide or sulfide, etc., or mixtures or compounds containing these may be advantageously employed in certain extractions. As mentioned the extraction may be carried out at atmospheric pressure, when high boiling, hydrogenated polynuclear aromatic compounds are utilized as solvents.

The time of extraction is not sharply critical and ranges from that period necessary to reach the desired extraction temperature to several hours. Generally, less than about an hour produces satisfactory results, with from about 30 minutes to an hour being preferred.

The distillation to recover the solvents employed in the extraction stage is conventional and is carried out to a degree sufficient to remove at least the bulk of the solvent employed, e. g., in the case of a tetralin-cresol solvent mixture, until temperature of the vapors reaches about 403° F. As mentioned above the recovery of solvent may be effected before destructive distillation of the extract residue mixture, or from the products of the destructive distillation.

The destructive distillation or coking of the extract-residue mixture is carried out under conventional conditions, i. e., in the absence of oxygen, generally at atmospheric pressure (although higher pressure may be used), and to a degree sufficient to remove at least the bulk of the volatile constituents of the distilland, including those formed by decomposition. Satisfactory temperatures for the coking step vary according to specific charges, but in general are between about the temperature at which most of the solvent has been removed and about the temperature at which most or all of the volatile matter has been driven off. Up to a temperature of about 750° F. volatile constituents already present in the extract-residue mixture are removed. Above about 750° F. decomposition takes place in the distilland. Accordingly, the coking step involves heating the distilland until a desired maximum somewhere above 750° F. is reached. Although a maximum of between 1100 and 1200° F. was employed in the specific examples, higher maximum temperatures, i. e., up to about 1800° F. may be utilized.

The silicone anti-foam material (when its presence is desired) may be added in relatively small proportions ranging from a few ten thousandths of a per cent up to about 1%. Larger proportions may be employed, but with no further advantages. An example of a satisfactory agent for this purpose is Dow Corning Silicone Fluid No. 200, a liquid polymer of a dialkyl silicone.

As has been stated, it is advantageous to confine the application of heat to the coking vessel during certain stages of the process to the top and sides of the vessel, namely, over the temperature range at which the greatest evolution of volatile material (other than solvent) occurs and at which the greatest tendency toward foaming manifests itself. This temperature range may vary according to specific samples of lignitic coal, but in general has been found to be between about 400° F. and 700° F. For any given charge

the proper temperatures may be determined from a trial run.

By means of this invention I have provided a process by which a good quality coke may be produced from the non-coking, lignitic coals. Another advantage of the process resides in the concurrent production of substantial amounts of valuable by-products, namely, liquid materials, boiling in the gasoline and fuel oil range. A further benefit produced by the invention is the elimination of the previously employed, difficultly carried out filtration of the viscous extract-residue mixture.

What I claim is:

1. The process of producing a strong, coherent, porous, lump coke from a lignitic coal comprising extracting the lignitic coal in the presence of hydrogen available at extraction conditions with a solvent selected from the group consisting of polynuclear aromatic compounds, hydrogenated polynuclear aromatic compounds and their mixtures with a phenolic compound, at elevated temperature effective to facilitate the extraction and at a pressure at least sufficient to retain reactants and reaction products, removing the solvent and destructively distilling the extract-residue mixture to drive off volatile material.

2. The process of producing a strong, coherent, porous, lump coke from a lignitic coal comprising extracting the lignitic coal in the presence of gaseous hydrogen with a solvent selected from the group consisting of polynuclear aromatic hydrocarbons, hydrogenated products thereof, and their mixtures with a phenolic compound, at elevated temperature effective to facilitate the extraction, at a substantial superatmospheric pressure, removing the solvent, and destructively distilling the extract-residue mixture to drive off volatile material.

3. The process of producing a strong, coherent, porous lump coke from a lignitic coal comprising extracting the lignitic coal with a solvent mixture containing a hydrogenated polynuclear aromatic hydrocarbon, at elevated temperature effective to facilitate the extraction and at a pressure at least sufficient to retain reactants and reaction products, removing solvent, and destructively distilling the extract-residue mixture to drive off volatile material.

4. The process of producing a strong, coherent, porous lump coke from lignitic coal comprising extracting the lignitic coal with a mixture of a hydrogenated polynuclear aromatic compound and a phenolic compound, at elevated temperature effective to facilitate the extraction and a pressure at least sufficient to retain reactants and reaction products, removing solvent, and destructively distilling the extract-residue mixture to drive off volatile material.

5. The process of producing a strong, coherent, porous lump coke from a lignitic coal comprising extracting the coal with a solvent containing tetralin at elevated temperature effective to facilitate the extraction and at a pressure at least sufficient to retain reactants and reaction products, removing solvent, and destructively distilling the extract-residue mixture to drive off volatile material.

6. The process of producing a strong, coherent, porous lump coke from a lignitic coal comprising extracting the coal with a solvent containing hydrogenated chrysene, at an elevated temperature effective to facilitate the extraction and not above the boiling point of the solvent, and at

atmospheric pressure, removing solvent, and destructively distilling extract-residue mixture to drive off volatile material.

7. The process of producing a strong, coherent, porous lump coke from a lignitic coal, comprising extracting the lignitic coal in the presence of hydrogen available at extraction conditions, with a solvent selected from the group consisting of polynuclear aromatic hydrocarbons, hydrogenated products thereof, and their mixtures with a phenolic compound, at elevated temperature effective to facilitate the extraction and at a pressure at least sufficient to retain reactants and reaction products, removing solvent, and destructively distilling the extract-residue mixture together with a foam inhibiting amount of a polymeric organo-silicon-oxide compound to drive off volatile material, but applying at least the major portion of the heat to the top and sides of the distillation vessel during the temperature range over which most of the volatile material is evolved, and recovering a dense, coherent coke and valuable liquid hydrocarbons boiling in the gasoline and fuel oil range.

8. The process of producing a strong, coherent, porous, lump coke from a lignitic coal comprising extracting the lignitic coal in the presence of hydrogen available at extraction conditions with a solvent selected from the group consisting of polynuclear aromatic compounds, hydrogenated polynuclear aromatic compounds and their mixtures with a phenolic compound at a temperature from about 480° F. to about 900° F. and at a pressure sufficient to retain reactants

and reaction products, removing the solvent, and removing volatile matter by destructively distilling the extract-residue mixture to a maximum temperature of up to about 1800° F.

9. The process of producing a strong, coherent, porous lump coke from a lignitic coal comprising extracting lignitic coal with a solvent containing tetralin and a phenolic compound, where the tetralin:phenolic compound ratio is from about 1:1 to about 5:1, and where the solvent:coal ratio is from about 1:2 to about 2:1, at a temperature from about 750° F. to about 860° F., at a pressure at least sufficient to retain the reactants and reaction products, removing the solvent and removing volatile matter by destructively distilling the extract-residue mixture to a maximum temperature of from about 750° F. to about 1800° F.

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