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(54) **SYSTEMS AND METHODS FOR REFINING COAL INTO HIGH VALUE PRODUCTS**

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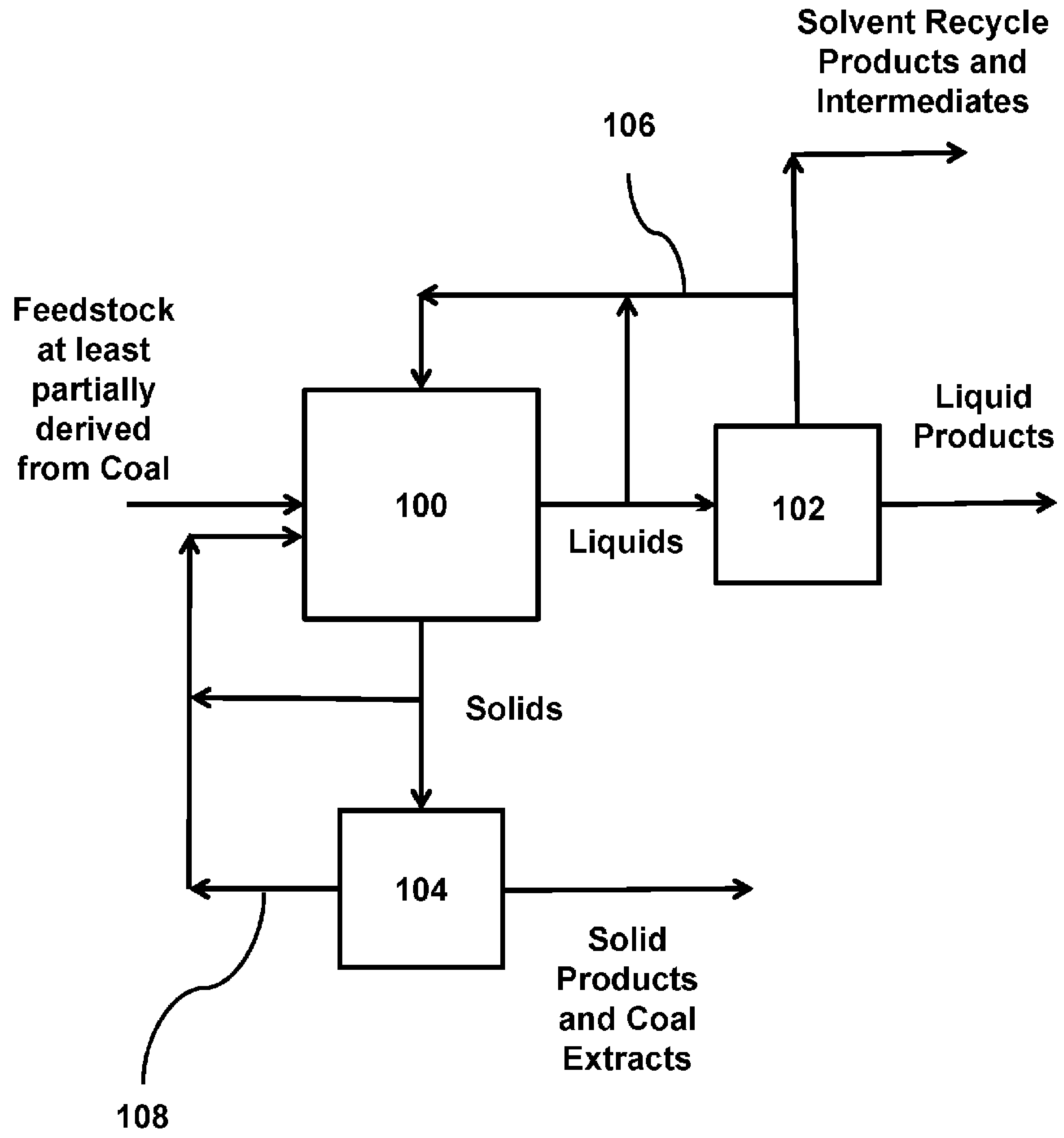
(57) **ABSTRACT**

Described herein are integrated thermochemical processes for the conversion of coal into high-value products using a combination of pyrolysis and solvent extraction. The described systems and methods are versatile and may be used to generate a variety of high value products including chemicals (aromatics, asphaltenes, napthenes, phenols, polyamides, polyurethanes, polyesters), polymer composite products (resins, coatings), graphitic products, agricultural materials, building materials, carbon fiber and other products that are substantially more valuable that the energy generated via combustion. Further, these systems and methods are specifically designed to be highly branched and highly flexible, allowing for a high selectivity and optimization for increasing the value of the products relative to the feedstock.



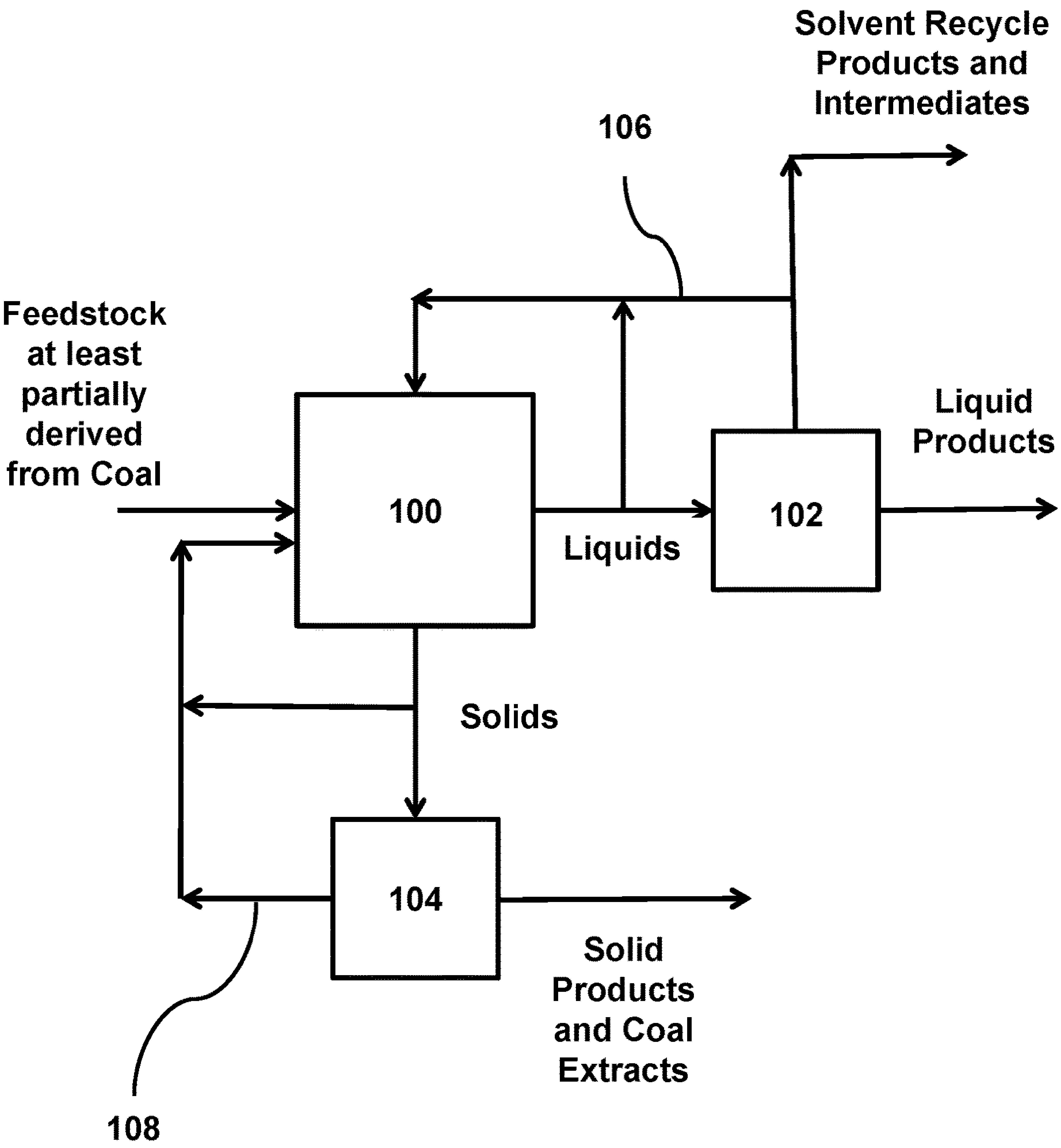

Solvent Recycle Products and Intermediates
106
Feedstock at least partially derived from Coal
100
Liquids
102
Liquid Products
Solids
104
Solid Products and Coal Extracts
108

FIG. 1

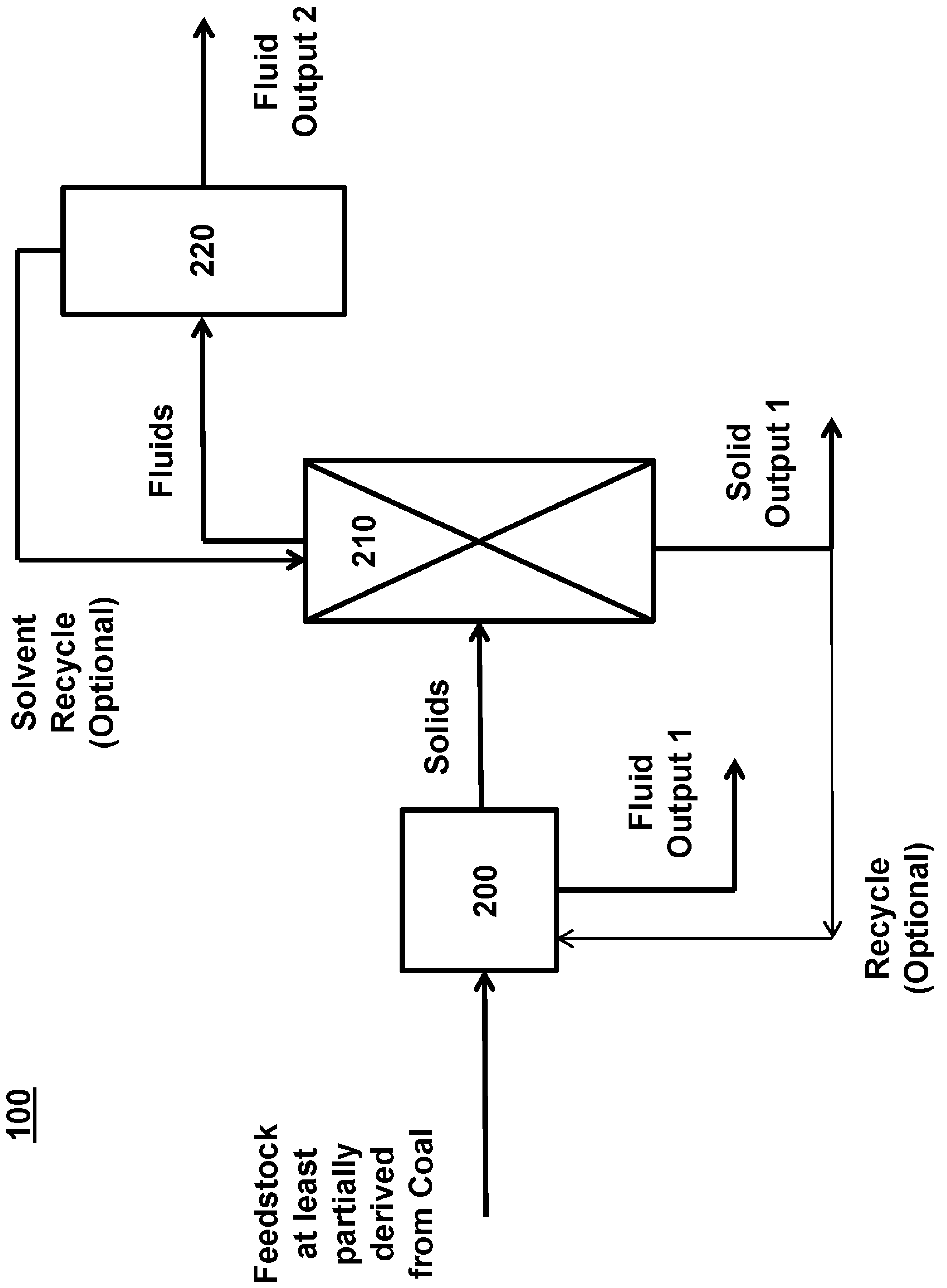

100
Feedstock at least partially derived from Coal
200
Fluid Output 1
Recycle (Optional)
Solids
210
Solid Output 1
Solvent Recycle (Optional)
Fluids
220
Fluid Output 2

FIG. 2

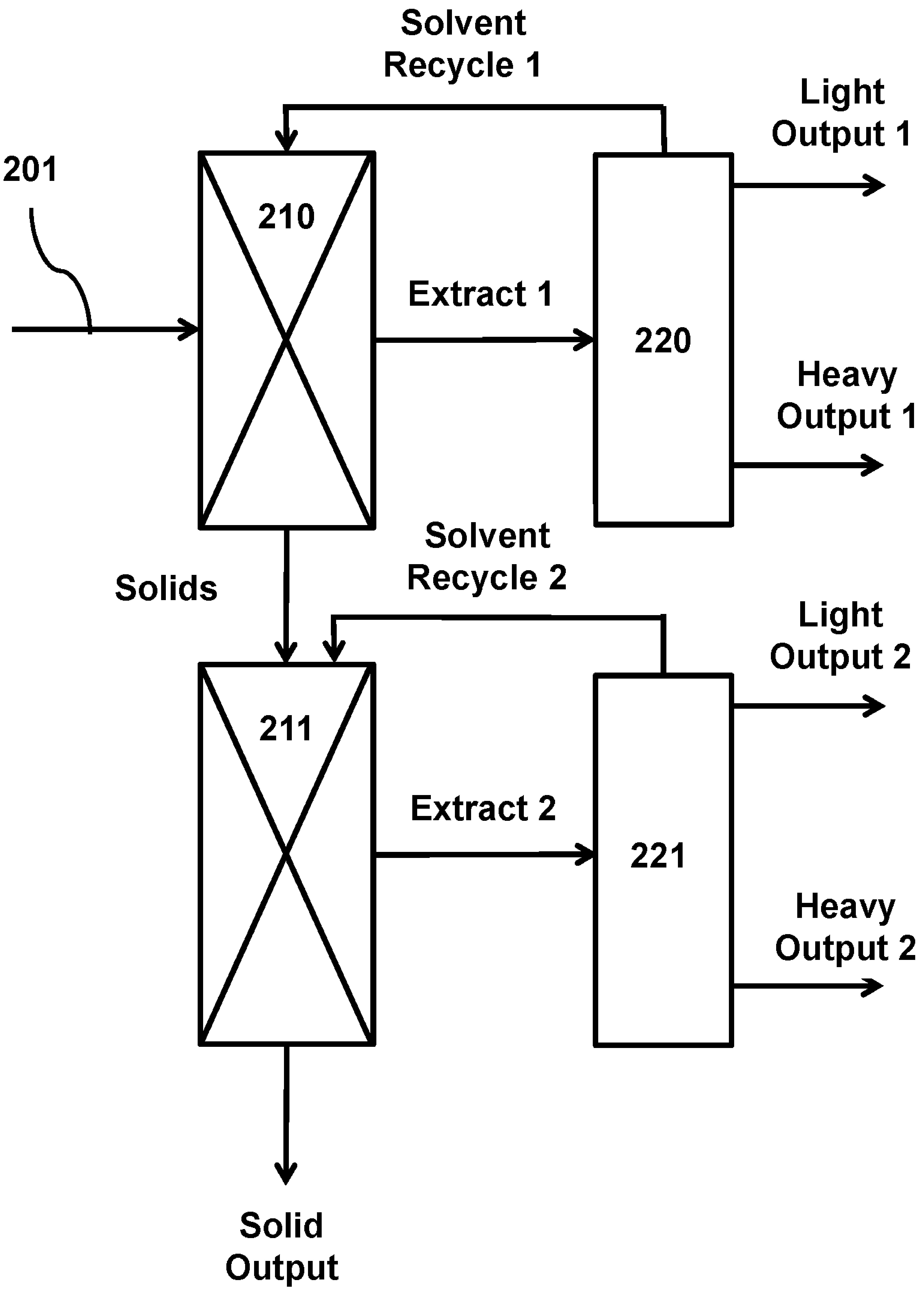

Solvent
Recycle 1
Light
Output 1
201
210
Extract 1
220
Heavy
Output 1
Solvent
Recycle 2
Solids
Light
Output 2
211
Extract 2
221
Heavy
Output 2
Solid
Output

FIG. 3

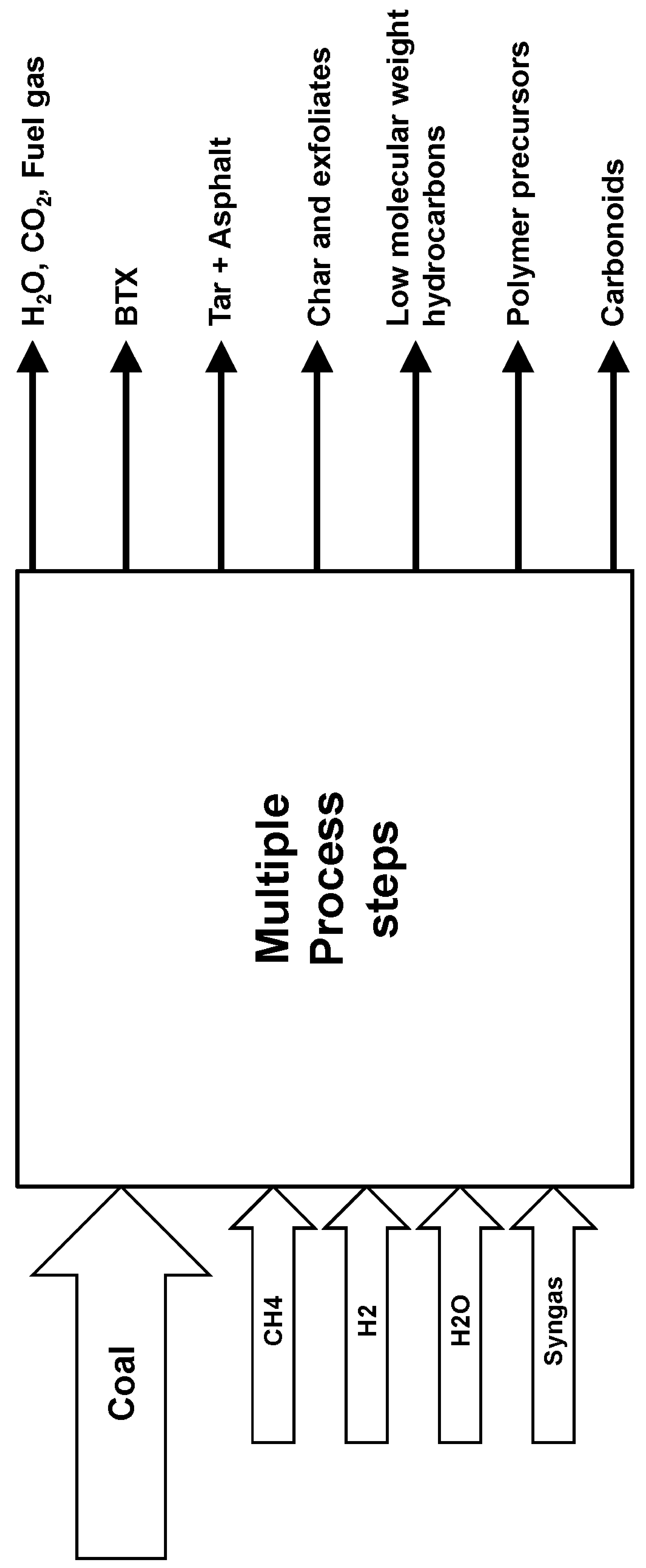

Coal
CH4
H2
H2O
Syngas
Multiple Process steps
H_2O, CO_2, Fuel gas
BTX
Tar + Asphalt
Char and exfoliates
Low molecular weight hydrocarbons
Polymer precursors
Carbonoids

FIG. 4

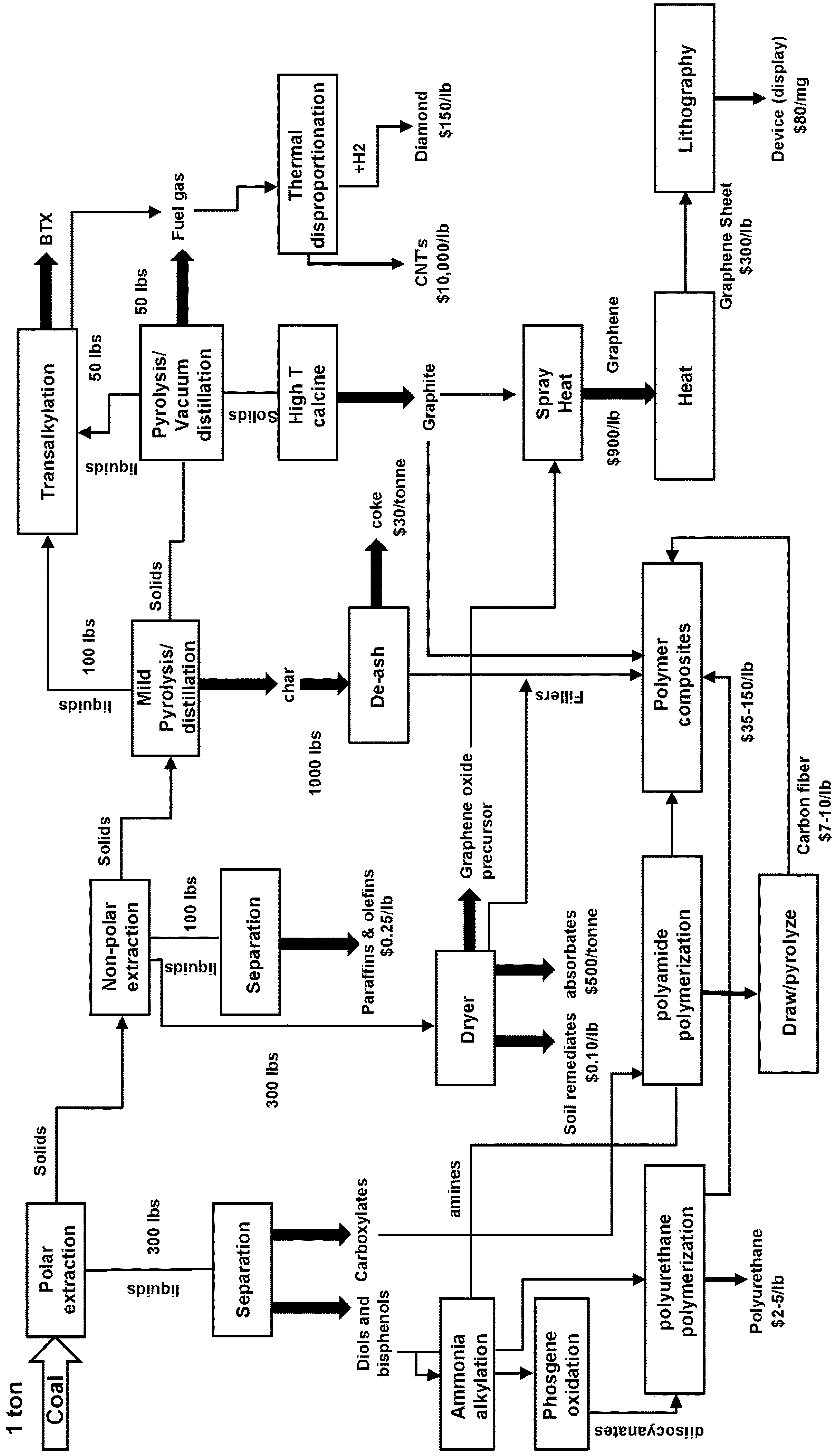

1 ton
Coal
Polar extraction
liquids
300 lbs
Separation
Diols and bisphenols
Carboxylates
Ammonia alkylation
Phosgene oxidation
diisocyanates
amines
polyurethane polymerization
Polyurethane $2-5/lb
Solids
Non-polar extraction
liquids
100 lbs
Separation
Paraffins & olefins $0.25/lb
300 lbs
Dryer
Soil remediates $0.10/lb
absorbates $500/tonne
Graphene oxide precursor
Fillers
polyamide polymerization
Draw/pyrolyze
Carbon fiber $7-10/lb
Polymer composites
$35-150/lb
Solids
Mild Pyrolysis/ distillation
liquids
100 lbs
char
1000 lbs
De-ash
coke $30/tonne
Solids
Transalkylation
BTX
liquids
Pyrolysis/ Vacuum distillation
50 lbs
50 lbs
Fuel gas
Solids
High T calcine
Graphite
Thermal disproportionation
+H2
Diamond $150/lb
CNT's $10,000/lb
Spray Heat
$900/lb
Graphene
Heat
Graphene Sheet $300/lb
Lithography
Device (display) $80/mg

FIG. 5

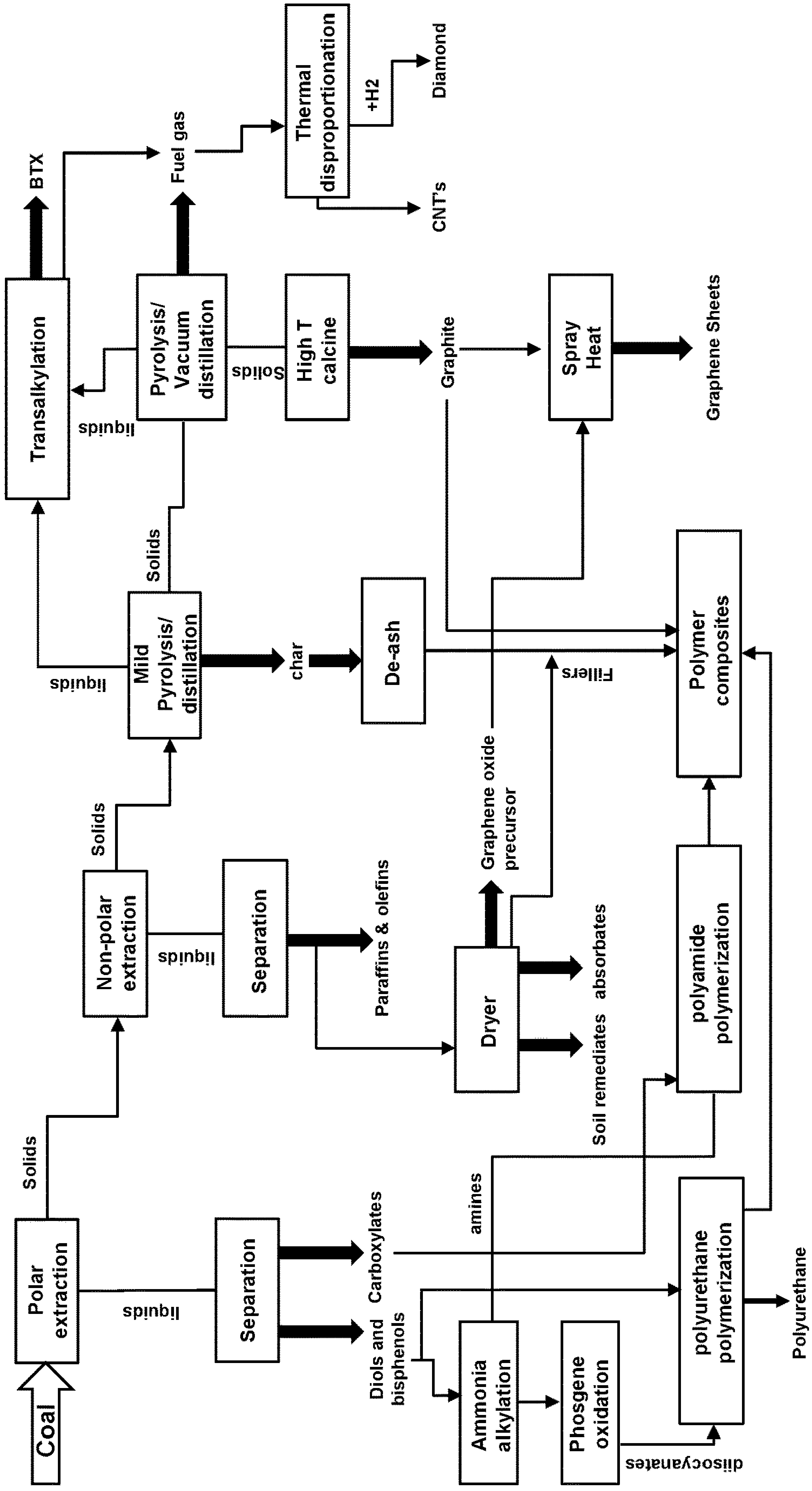

Coal
Polar extraction
liquids
Separation
Diols and bisphenols
Carboxylates
Solids
Non-polar extraction
liquids
Separation
Paraffins & olefins
Solids
Mild Pyrolysis/ distillation
liquids
Solids
char
De-ash
Transalkylation
liquids
Pyrolysis/ Vacuum distillation
Solids
High T calcine
Graphite
Spray Heat
Graphene Sheets
BTX
Fuel gas
Thermal disproportionation
+H2
Diamond
CNT's
Dryer
Soil remediates
absorbates
Graphene oxide precursor
Fillers
Polymer composites
polyamide polymerization
amines
Ammonia alkylation
Phosgene oxidation
diisocyanates
polyurethane polymerization
Polyurethane

FIG. 6

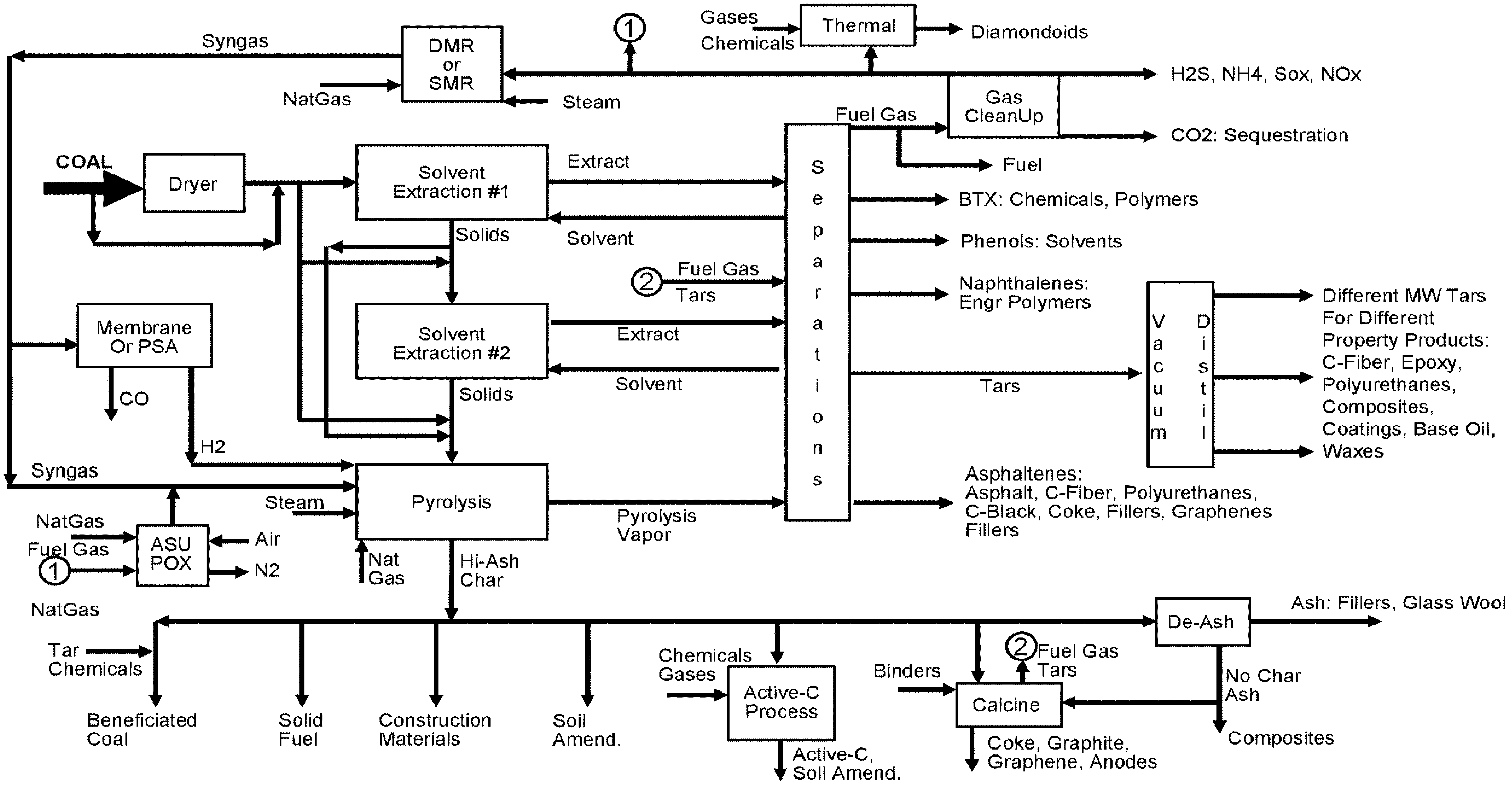

Syngas
DMR or SMR
NatGas
Steam
①
Gases
Chemicals
Thermal
Diamondoids
H2S, NH4, Sox, NOx
Gas CleanUp
CO2: Sequestration
Fuel Gas
Fuel
COAL
Dryer
Solvent Extraction #1
Extract
Solvent
Solids
S e p a r a t i o n s
BTX: Chemicals, Polymers
Phenols: Solvents
② Fuel Gas
Tars
Naphthalenes: Engr Polymers
Membrane Or PSA
CO
H2
Solvent Extraction #2
Extract
Solvent
Solids
Tars
V a c u u m
D i s t i l l
Different MW Tars For Different Property Products: C-Fiber, Epoxy, Polyurethanes, Composites, Coatings, Base Oil, Waxes
Syngas
Steam
Pyrolysis
Pyrolysis Vapor
Asphaltenes: Asphalt, C-Fiber, Polyurethanes, C-Black, Coke, Fillers, Graphenes Fillers
NatGas
Fuel Gas
①
ASU POX
Air
N2
Nat Gas
Hi-Ash Char
NatGas
De-Ash
Ash: Fillers, Glass Wool
Tar Chemicals
Beneficiated Coal
Solid Fuel
Construction Materials
Soil Amend.
Chemicals Gases
Active-C Process
Active-C, Soil Amend.
Binders
② Fuel Gas Tars
Calcine
Coke, Graphite, Graphene, Anodes
No Char Ash
Composites

FIG. 7

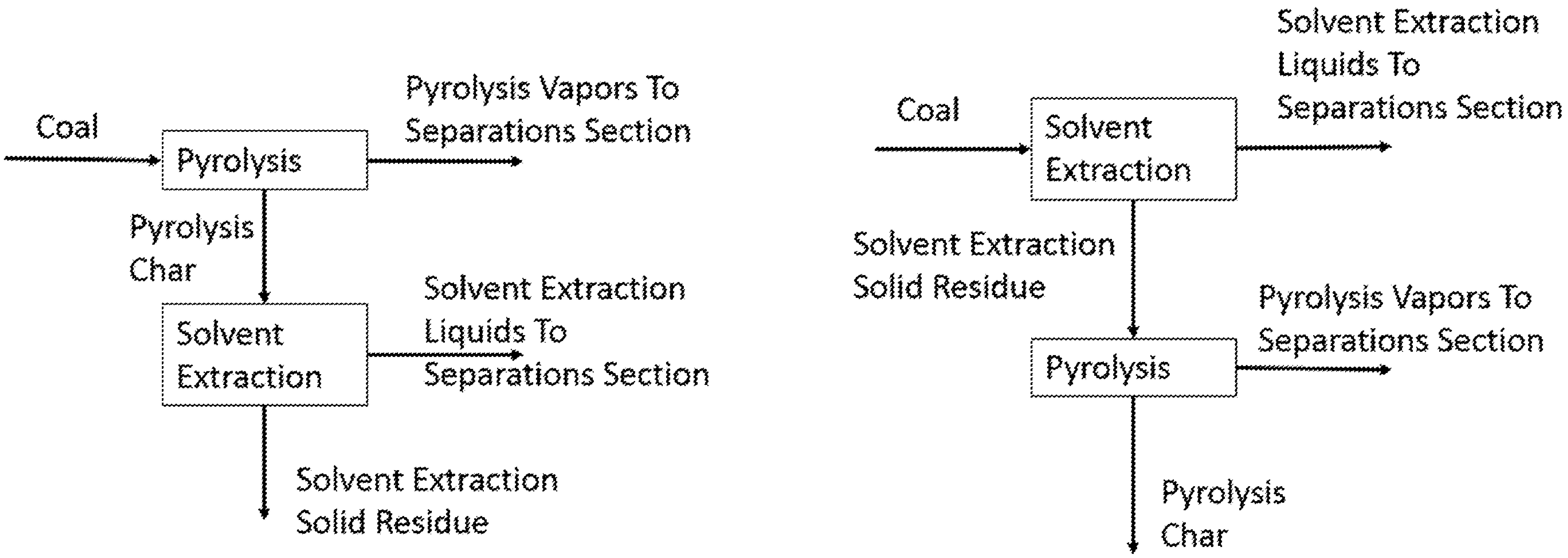

Coal
Pyrolysis
Pyrolysis Vapors To Separations Section
Pyrolysis Char
Solvent Extraction
Solvent Extraction Liquids To Separations Section
Solvent Extraction Solid Residue
Coal
Solvent Extraction
Solvent Extraction Liquids To Separations Section
Solvent Extraction Solid Residue
Pyrolysis
Pyrolysis Vapors To Separations Section
Pyrolysis Char

FIG. 8

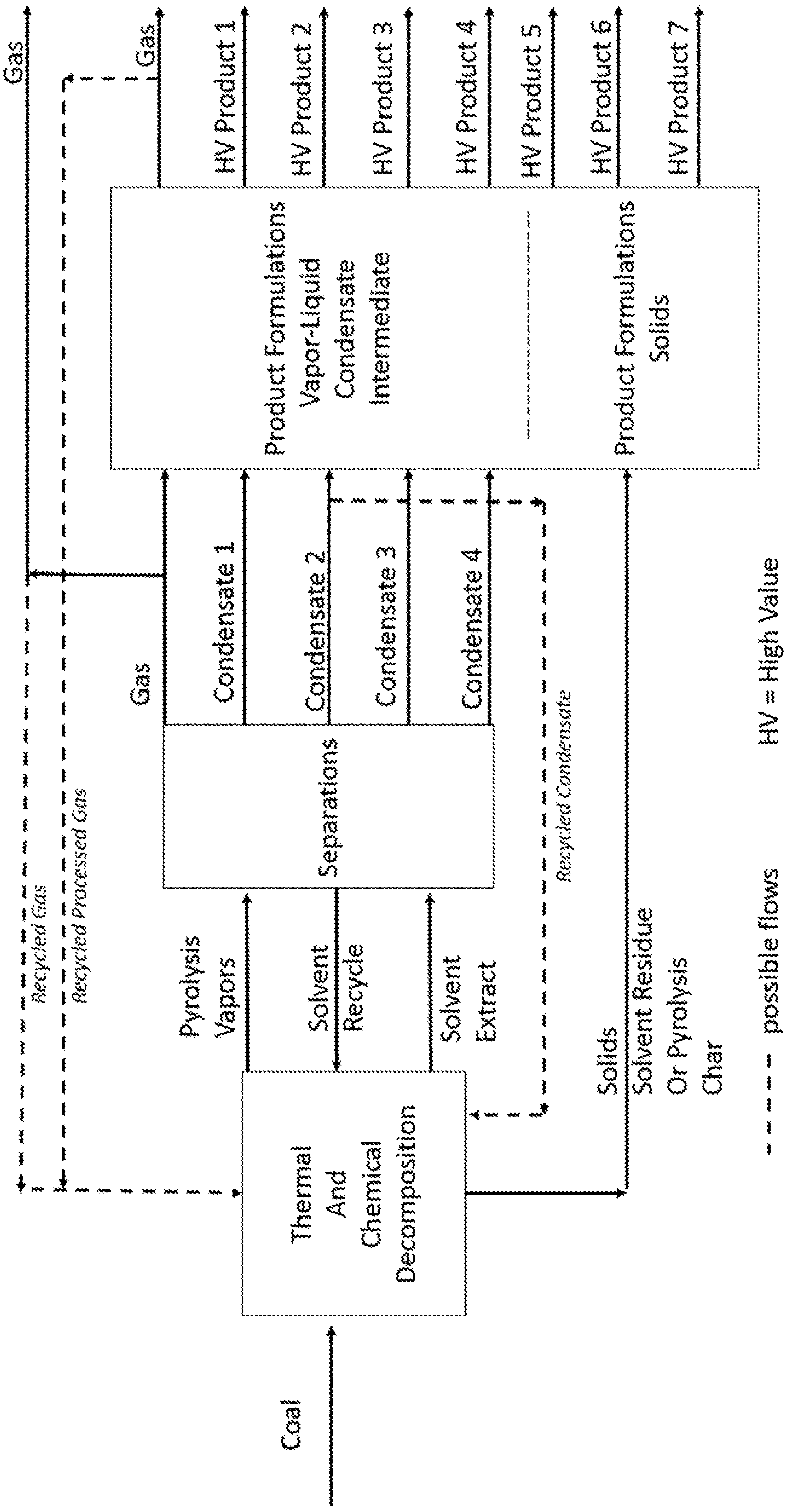

Coal
Thermal And Chemical Decomposition
Pyrolysis Vapors
Solvent Recycle
Solvent Extract
Solids
Solvent Residue Or Pyrolysis Char
Recycled Gas
Recycled Processed Gas
Recycled Condensate
Separations
Gas
Condensate 1
Condensate 2
Condensate 3
Condensate 4
Gas
Gas
Product Formulations Vapor-Liquid Condensate Intermediate
Product Formulations Solids
HV Product 1
HV Product 2
HV Product 3
HV Product 4
HV Product 5
HV Product 6
HV Product 7
- - - - possible flows
HV = High Value

FIG. 9

SYSTEMS AND METHODS FOR REFINING COAL INTO HIGH VALUE PRODUCTS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This patent application claims the benefit of and priority to U.S. Provisional Patent Application No. 62/557,804 filed Sep. 13, 2017 which is hereby incorporated by reference to the extent not inconsistent herewith.

BACKGROUND OF THE INVENTION

[0002] Coal mining and production represents a large, valuable industry in both the United States and abroad. The vast majority of this coal is combusted to generate energy. Currently, there is a great deal of economic and political pressure on the building of new coal-fired power plants. Accordingly, to further utilize coal beyond combustion, it becomes increasingly attractive to investigate use as a feedstock for other processes, including for the production of chemicals, plastics, building materials and products which may have significantly higher value than that of the energy produced by power plants.

[0003] Research and development into coal as a feedstock for the generation of chemicals and other materials has been around for more than 50 years. Interest in this field has typically increased during periods in which traditional petroleum feedstocks have become expensive due to high oil prices, such as in the 1970's. For example, U.S. Pat. No. 4,346,077 discusses pyrolysis of coal to generate liquid hydrocarbons and vapors. U.S. Pat. No. 9,074,139 describes generation of aromatic compounds from coal utilizing liquefaction and hydrocracking. Common amongst these references and most coal conversion technology is that coal is being converted into coal tars to mimic petroleum hydrocarbons in such a way that it can then be processed through a petroleum refinery. Coal, which generates a greater amount of solid products and typically contains a high sulfur content and some metals, often makes a relatively poor substitute for processes designed for oil-based feedstocks.

[0004] It can be seen from the foregoing that there remains a need in the art for systems and methods for the deliberate, thermochemical conversion of coal into intermediate and finished high-value products, thereby generating materials that are far more valuable than the equivalent coal-based energy produced via combustion. Further, separation and process systems and methods are needed that are specifically tailored and/or customized to coal and coal-based feedstocks to achieve effective transformation into products, that consider yields, efficiency, conversion rates and the manufacture of distinguished goods that can be sold.

BRIEF SUMMARY OF THE INVENTION

[0005] Described herein are integrated thermochemical processes for the deliberate decomposition, extraction and conversion of coal into high-value products and goods using a combination of pyrolysis and solvent extraction. The described systems and methods are versatile deliberate and may be used to generate a variety of intermediate and finished high value products including chemicals (aromatics, asphaltenes, napthalenes, phenols and precursors for the production of polyamides, polyurethanes, polyesters, graphitic materials), polymer composite products (resins, coatings, adhesives), agricultural materials, building materials, carbon fiber, graphene products and other materials that are substantially more valuable that the energy generated via combustion. Further, these systems and methods are specifically designed to be highly branched (i.e. process steps that together are amenable to produce wide ranging product types and specifications from the same feedstock), as well as being synergistic (e.g. permitting combining resin systems produced from coal with solid carbon material derived from coal to make composite materials). Thus the systems and methods are highly adaptive to markets and responsive to product demand. Thus, allowing for a high selectivity and optimization for increasing the value of the actual products relative to the feedstock. Some of these products may be coal extracts such as metals and rare earth elements.

[0006] The provided thermochemical processes convert a large portion of the coal feedstock into and extracts from coal value added products and may focus on converting a high percentage (e.g. greater than 50% dry basis) of the solid material into fluids. These systems and methods may avoid expensive, energy intensive hydrocracking and hydrotreating processes. The thermochemical processes described herein use an integrated combination of thermal and chemical processes to provide controlled and deliberate conversion of coal and extraction from coal into a selective and switchable mix of high-value products that may be optimized to achieve profitable manufacturing motivated by the total value of goods generated.

[0007] In an aspect, provided is a method for converting coal into a plurality of high value coal products comprising: i) providing a feedstock, wherein the feedstock is at least partially derived from coal; ii) processing the feedstock, wherein the processing step includes a combination of pyrolysis and solvent extraction, wherein the pyrolysis and solvent extraction are integrated and carried out under conditions for generating a plurality of high value coal products. The percentage of high value coal products that are liquid at standard temperature and pressure may be greater than or equal to 50% dry basis, greater than or equal to 60%, or optionally, greater than or equal to 70%. The step of processing may be highly branched, discriminating and wide ranging, yet highly selective.

[0008] Pyrolysis is generally used in the described systems to reduce the size or length of the complex molecules commonly found in coal and to concentrate extracts. Pyrolysis as described herein may refer to flash pyrolysis, for example, having small residence times (on the order of seconds) at high temperatures. The pyrolysis processes described herein may, in some embodiments, specifically exclude the use of a catalyst and, in some embodiments, specifically include the use of a catalyst. The pyrolysis processes described herein may, in some embodiments be highly selective.

[0009] Pyrolysis may be a single stage pyrolysis, multiple single stage pyrolysis, a single multistage pyrolysis, multiple multistage pyrolysis or a combination of single stage and multistage pyrolysis steps. Each pyrolysis or pyrolysis step may independently be performed at a pressure selected from the range of 0.5 atm to 15 atm, 0.9 atm to 15 atm, or 0.9 atm to 10 atm. Each pyrolysis or pyrolysis step may be performed at a temperature selected from the range of 400° C. to 1200° C., 750° C. to 1200° C., or optionally, 900° C. to 1100° C. In an embodiment, the residence time for pyrolysis is selected over the range of 30 minutes to 0.1 seconds and optionally less than or equal to 10 seconds, 5 seconds, 2 seconds, or 1 second. Pyrolysis may be integrated with solvent extraction, as a pretreatment or post treatment. In each pyrolysis or pyrolysis step may independently be performed at a pressure selected from the range of 0.5 atm to 15 atm, 0.9 atm to 15 atm, or 0.9 atm to 10 atm.

[0010] Solvent extraction may generate a mass percentage of gas, excluding water vapor, less than or equal to 25%, less than or equal to 15%, less than or equal to 10%, less than or equal to 5%, or optionally, less than or equal to 3%. Solvent extraction may generate a mass percentage of liquid, which may include or exclude the solvent itself up to 100%, which itself becomes a precursor or intermediate for further processing into goods and products. Pyrolysis may be performed in nitrogen, air or hydrogen-donating environment such as in the presence of hydrogen gas, methane, syngas or any combination thereof. Pyrolysis may be flash pyrolysis.

[0011] Solvent extraction is generally used to remove and/or separate various components of the solid feedstock including the intermediates and end products. It should be noted, that in some instances solvent extraction does facilitate chemical reactions including conversion of solid material into liquids and may chemically alter the various components being processed. Various solvents known in the art may be used, including aliphatic, aromatic, hydrogen donating, non-polar solvents, polar solvents and ionic liquid solvents. Solvent extraction may include multistage extraction and multiple solvent extraction steps ahead or following pyrolysis. Solvent extraction may include super critical fluid steps. Solvent extraction may also utilize fractionation, or the use of multiple solvent extraction steps at different temperatures and pressures. Various uses of solvent recovery, including solvent recycling may provide additional efficiency and cost savings in addition to the solvent being a precursor or intermediate product for further processing in itself.

[0012] Solvent extraction, as described herein, may be performed with at least one liquid solvent. The at least one solvent may be selected from the group consisting of an aliphatic solvent, an aromatic solvent, a polar solvent, a hydrogen donating solvent, an ionic liquid solvent and any combination thereof. Solvent extraction may use at least two liquid solvents. The first solvent may be a polar solvent, a combination of solvents which may include polar and aromatic solvents applied separately. The second solvent may be a hydrogen donating solvent or vice versa. The solvent extract itself may be an intermediate that is further processed into a finished product.

[0013] Solvent extraction may be a single stage solvent extraction, multiple single stage solvent extractions, a single multistage solvent extraction, multiple multistage solvent extractions or a combination of single stage and multistage solvent extractions. Solvent extraction may be performed at a temperature less than the critical temperature of the solvent. Each Solvent extraction or step may independently be performed at less than or equal to 400° C., less than or equal to 350° C., or optionally, less than or equal to 300° C. Solvent extraction may generate a mass percentage of gas, excluding water vapor, less than or equal to 10%, less than or equal to 5%, or optionally, less than or equal to 1%.

[0014] Solvents as described herein may comprise tetralin (1,2,3,4-Tetrahydronaphthalene), 1-methyl-napthalene, toluene, dimethylformamide (DMF) or any combination thereof. A solvent may be impure, for example, due to recycle or separation inefficiencies.

[0015] The described systems and method are flexible and the solvent extraction step may be performed prior to the pyrolysis step and vice versa. Further, systems that are more complex may utilize multiple pyrolysis steps and/or multiple solvent extraction steps in any combination, for example, a first pyrolysis step followed by a first solvent extraction and then a second pyrolysis step. Additionally, recycle streams may be utilized such that a portion the output from one step (either pyrolysis or solvent extract) may be recycled and used as in input or as a portion of an input for a previous step, subsequent step or current step. The solvent extraction and pyrolysis steps may be considered as integrated achieving results that pyrolysis and/or solvent extraction cannot achieve alone.

[0016] The solvent extraction may be performed upstream of the pyrolysis. The pyrolysis may be performed upstream of the solvent extraction. A portion of products from the pyrolysis step may be recycled to the solvent extraction. A portion of products from the solvent extraction may be recycled to the pyrolysis or sent for further downstream processing. The processing step may comprise multiple solvent extractions and solvents from a later solvent extraction may be recycled to an earlier solvent extraction or the pyrolysis step.

[0017] The primary feedstocks described herein are generally coal or coal-based, including run of mine coal and/or coal, which may be physically, chemically and/or thermally pre-processed which may include drying and vapors recovery. Pre-processing may include pulverizing, de-ashing and/or drying. The described systems and methods are flexible and may be used with any primary feedstock including lignite, subbituminous and bituminous coal. Secondary feedstocks inclusions may include other hydrocarbon sources such as biomass and oil shale and/or inclusion of secondary recycle streams from downstream processes e.g. syngas and other reactive mineral resources such as trona.

[0018] High value coal products described herein have a monetary or economic value significantly higher than the value of the energy produced by burning or combusting the primary feedstock. High value coal products may comprise a minority manufacture of fuels products and/or blending components, such as less than or equal to 10% fuel products and/or blending products, less than or equal to 5% fuel products and/or blending products, or optionally, less than or equal to 3% fuel products and/or blending products. High value coal products may comprise polymers or polymer precursors. High value coal products may comprise polyurethane. High value coal products may comprise composite polyurethane foam. High value coal products may comprise polyamides. High value coal products may comprise polyesters. High value coal products may comprise aromatics. High value coal products comprise benzene, toluene, xylenes (including isomers), phenols, cresols, xylenols (including isomers), naphthenols, C9 single ring aromatics (including isomers), C10 single ring aromatics (including isomers) or any combination thereof. High value coal products may comprise paraffins, olefins, asphaltenes, napthenes or a combination thereof. High value coal extractive products may include metals and rare earth elements.

[0019] High value coal products may comprise asphaltenic intermediates and/or finished products. High value coal products may comprise road paving and roofing intermediates, additives or finished products. High value coal products may comprise coal tar, distillates, pitch, asphalt, graphitic materials, carbon fibers or any combination thereof. High value coal products may comprise soil amendments and fertility products. High value coal products may comprise building materials. A significant portion of the high value coal products may be solids, for example, greater than or equal to 10% solids, greater than or equal to 20% solids, or optionally, greater than or equal to 30% solids. The solids may be converted to graphitic materials, construction materials, composite materials, liquid additives or any combination thereof when combined a resin, liquid or other bi-product generated by the methods described herein. High value products may include syngas, urea, CO_2 and/or acetylene.

[0020] In an aspect, provided is a method for converting coal into a plurality of high value coal products comprising: i) providing a primary feedstock at least partially derived from coal; ii) processing the primary feedstock, wherein the processing sequence is a) a pyrolysis step, wherein the pyrolysis step is performed in less than or equal to 10 seconds performed in a hydrogen rich atmosphere; and b) a solvent extraction step, wherein the solvent extraction step is performed with at least one liquid solvent, wherein the liquid solvent is selected from the group consisting of: a polar solvent, and/or a hydrogen donating solvent and/or any combination thereof; c) wherein the pyrolysis step is the first process step carried out on the primary feedstock and wherein the solvent extraction process is the second process step carried out on the solid char produced from the pyrolysis; d) wherein the pyrolysis and solvent extraction process are integrated and carried out under conditions for generating a plurality of high value coal products.

[0021] The pyrolysis step may be a flash pyrolysis process. The solvent extraction step may be a single stage solvent extraction, multiple single stage solvent extractions, a single multistage solvent extraction, multiple multistage solvent extractions or a combination of single stage and multistage solvent extractions. The solvent extraction step may use two or more solvents. Processing the feedstock may further comprise one or more separation steps occurring after the pyrolysis, after the solvent extraction process or in between multiple solvent extractions.

[0022] Without wishing to be bound by any particular theory, there may be discussion herein of beliefs or understandings of underlying principles relating to the devices and methods disclosed herein. It is recognized that regardless of the ultimate correctness of any mechanistic explanation or hypothesis, an embodiment of the invention can nonetheless be operative and useful.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING(S)

[0023] FIG. **1** provides an overview of the described process including additional post-processing to generate liquid and solid products.

[0024] FIG. **2** provides an example processing step where pyrolysis is followed by solvent extraction.

[0025] FIG. **3** provides an example of a multistage solvent extraction step where two different solvents are used to increase extraction effectiveness.

[0026] FIG. **4** provides an overview including inputs and outputs.

[0027] FIG. **5** is an example of a highly branched, highly selective process utilizing solvent extraction and pyrolysis.

[0028] FIG. **6** is an example of a highly branched, highly selective process utilizing solvent extraction and pyrolysis.

[0029] FIG. **7** provides an example overview with high detail regarding products and additional processes.

[0030] FIG. **8** provides additional examples of integrated, multistage processing steps.

[0031] FIG. **9** provides example thermochemical processing steps.

DETAILED DESCRIPTION OF THE INVENTION

[0032] In general, the terms and phrases used herein have their art-recognized meaning, which can be found by reference to standard texts, journal references and contexts known to those skilled in the art. The following definitions are provided to clarify their specific use in the context of the invention.

[0033] As used herein, "feedstock at least partially derived from coal" refers to a solid, powder, slurry, liquid, fluid or other material that has been generated from a raw coal source. For example, raw coal may be crushed into a powder prior to processing. The feedstock may have various physical, thermal and chemical pretreatments known in the art to further facilitate processing of the feedstock, for example, by flash pyrolysis and solvent extraction. The feedstock may also act as a recycled stream from one or more of the downstream processes or intermediates (e.g. solid material remaining after solvent extraction) so that additional products, such as liquid products, may be promoted by reprocessing less valuable or unwanted intermediate products.

[0034] "Coal" refers to predominately solid hydrocarbons that may contain some amount of fluid material. Coal is generally composed of hydrogen, carbon, sulfur, oxygen and nitrogen. Coal, as described herein, may refer to bituminous coal, subbituminous coal and lignite. Coal may also refer to ash or peat.

[0035] "Flash Pyrolysis" as described herein, refers to a thermal process in which a feedstock or intermediate product is exposed to sufficient energy to rapidly heat the feedstock or intermediate. Flash pyrolysis may, for example, provide heat or heat the material being processed to temperatures of greater than 750° C., greater than 900° C., greater than 1050° C., or optionally, greater than 1200° C. Flash pyrolysis may refer to a heating or resonance time of less than 60 seconds, less than 10 seconds, less than 5 seconds, less than 1 second, or optionally, less than 0.5 seconds. Flash pyrolysis may be performed in a vacuum, in the presence of air, or optionally, in the presence of a purified gas such as hydrogen or methane or syngas. It may also be performed in an inert atmosphere notably at very high temperatures greater than 1200° C.

[0036] "Solvent extraction" refers to the process of flowing a liquid solvent through or across a feedstock or intermediate product to facilitate the extraction components of the material via chemical reaction and/or mass transfer via solubility in the solvent. As described herein, solvent extraction may utilize one or more solids in one or more solvent extraction steps, including in multistage solvent extractions in which the same or similar solvents are repeatedly used on a materials. Solvents, as described herein, may be mixtures including mixtures of liquid hydrocarbons generated by the processes described herein. Solvents, as described herein, may be mixtures of a number of solvents. Solvents may be recycled and reused as is known in the art. Solvent extraction may be at subcritical temperatures. Solvent extraction may be performed at reduced pressures, atmospherics pressures or increased pressures.

[0037] "Solvent" as described herein refers to a liquid or a mixture of liquids or cocktails having solubility with regard to hydrocarbons or other species and molecules present in coal. Solvent may refer to a complex mixture of liquids, including hydrocarbon mixtures generally defined by boiling point ranges. Solvents may be polar, paraffinic, aromatic, alcohol, ionic, and/or hydrogen-donating in nature. In embodiments utilizing two or more solvents, solvents may be distinguished by composition, additives, molecular design, boiling point ranges or a combinations thereof.

[0038] "High Value Coal Products" describe chemicals and materials (both solid and liquid) generated by the processes described herein that are more valuable than the coal or feedstock at least partially derived from coal. High value coal products may refer to liquid products generated from predominately solid coal. The high value coal products described herein may have a 1.5×, 2×, 3×, 5×, 10×, or optionally, at least 50× monetary value in comparison with the coal or raw coal material provided in the feedstock. High value coal products may refer coal products that are 1.5×, 2×, 3×, 5×, 10×, or optionally, at least 50× more valuable than the energy that would be produced via burning of the coal. High value coal products may refer to products that are not fuel (e.g. created for the purpose of burning to generate energy). Examples of high value coal products include polymers (e.g., polyurethane, polyesters, polyamides), high value chemicals (BTX, paraffins, olefins, asphaltenes), composite materials, carbon fiber, graphene, building materials, road, paving and roofing materials and soil amendments. High value coal products may represent a fraction of the total material converted from the feedstock, for example, 50% of the total products on a dry basis, 70% of the total products on a dry basis, 80% of the total products on a dry basis, or optionally, 90% of the total products on a dry basis.

[0039] "Hydrogen rich environment" refers to an atmosphere comprising a large composition of hydrogen gas. Hydrogen rich environment may refer to an atmosphere comprising greater than or equal to 50 mole percent hydrogen, or in some embodiments, greater than or equal to 70 mole percent hydrogen. Hydrogen rich environment may refer to the atmosphere or conditions of a chamber or vessel in which pyrolysis is performed.

[0040] "Inert atmosphere" refers to an environment in which the gas phase is chemically inactive with the feedstock(s) present.

[0041] Pressure values described herein are provided as absolute pressure values, unless otherwise indicated.

[0042] The following examples further illustrate the invention but, of course, should not be construed as in any way limiting its scope.

Example 1—Coal Refining Process Overview

[0043] This example demonstrates a high-level overview of methods for the thermochemical decomposition of coal or a coal-based feedstock into deliberately selected high value products. FIG. **1** provides an overview schematic. In FIG. **1**, a feedstock at least partially derived from coal is feed into a processing step **100** that comprises pyrolysis and solvent extraction. Generally, the steps of pyrolysis and solvent extraction may occur in any order and may include multistage processes, additional steps of pyrolysis and/or solvent extraction, recycle streams and separations. From a process and method perspective, the solvent extraction and pyrolysis steps are integrated. The primary processing step **100** generates at least one solid output and liquid output, but may generate multiple solid and liquid output streams based on the configuration of the primary processing step **100**. In some cases, liquids will undergo additional liquid processing **102**, with the option of liquid recycle streams **106** returning specific liquid fractions to the primary processing **100**. In some cases, liquid recycle streams **106** including solvent recycle streams may be useful as intermediates to downstream processes or as products and may be separately sold or processed. Similarly, solids may under additional solid processing **104**, with optional recycle streams **104**. The end result is at least one high value liquid product and at least one high value solid product, although typically the described processes will generate a variety of high value products as well as lower value products (relative to feedstock cost) which may or may not be re-processed or sold.

[0044] An example of the processing step **100** is provided in FIG. **2**. First, the coal-based feedstock is treated via pyrolysis **200** reduce carbon chain length and liquefy or vaporize a portion of the feedstock. In this example, pyrolysis is performed at 400-1200° C. and at atmospheric pressure. Flash pyrolysis (e.g. resonance time of less than 1 minute) or pyrolysis with low resonance times (e.g. less than 15 minutes) may be used to increase efficiency, change product make and yields and/or decrease processing time while reducing energy requirements and, therefore, costs. The fluids from the pyrolysis process **200** may be either further processed (e.g. separated, polymerized, etc.) in downstream operations. The solids from the pyrolysis process **200** are sent to a solvent extraction unit **210**. Solvent extraction **210** further removes fluid components from the solid materials and may provide some chemical reaction such as reducing carbon chain length, increasing the ratio of hydrogen/carbon or interacting with sulfur and oxygen bonds and recovery of metals and rare earth elements. Remaining solids from the solvent extraction step **210** may be further treated as described herein, recycled through the process for additional conversion into lighter compounds or converted into other high value products. The fluid stream from the solvent extractor **210** may be separated, for example, in a distillation column **220**. The fluid stream may be split into one or more product streams based on volatility and solvent may be recovered and returned to the solvent extractor **210**. FIG. **8** provides additional examples of integrated, multistage processing steps and further illustrates the versatility in ordering of the various process steps.

Example 2—Pyrolysis

[0045] Pyrolysis used in the described systems and methods provides for the thermal decomposition of complex hydrocarbons found in coal and helps convert a portion of the solid coal materials into liquids and vapors. Pyrolysis as described herein is generally performed at a high temperature while being low enough to avoid combustion, for example, greater than 400° C., greater than 800° C., or optionally, greater than 1000° C. Further, to increase efficiency and reduce energy costs, pyrolysis of the described methods has generally low residence times, for example, less than 1 hour or in some cases less than 15 minutes. Some embodiments of the present invention utilize flash pyrolysis which may have a residence time less than 1 minute, or preferably less than 15 seconds. The described pyrolysis steps may be performed at or near atmospheric pressure or in a pressurized environment, including in some embodiments, in the presence of a hydrogen-rich gas including hydrogen gas, methane, natural gas or syngas.

[0046] Specific pyrolysis parameters are dependent on the input or feed stream. For example, in embodiments where pyrolysis is the first step in the described methods, the feed will be primarily coal or coal-derived material. However, in cases in which one or more solvent extractions are performed, the remaining solid material may have significantly different compositions and process parameters will need to be altered accordingly.

[0047] Coal pyrolysis experiments were performed on Cordero Rojo sub-bituminous coal. 25 g of coal was dried overnight at 100° C. under argon. The dry coal weight was determined and this becomes the basis for the yield calculations below. Then the contents were heated to 500° C. in a vertical tube furnace for 40 minutes. The generated pyrolysis vapors were sent to a cold trap at 0° C. to condense the tars and vent the remaining gas.

[0048] Below are weight-based yield results for dry coal based on the experimental procedure above:

TABLE 1

Weight-based yield results for pyrolysis

	Yield %	Notes
Solid Char Yield %	79.1	Char Weight * 100 Dry Coal Weight
Tar (liquid) Yield %	10.5	Cold Trap Liquid Tar Weight * 100 Dry Coal Weight
Gas Yield %	10.4	By difference

Example 3—Solvent Extraction

[0049] Solvent extraction provides an effective, cost efficient way to recover desirable and valuable fluid components from a predominately solid feedstock or intermediate. Additionally, selection and design of solvents may provide some chemical reactivity and may reduce the size or length of the complex hydrocarbon molecules often found in coal and or permit the economic recovery of metals and rare earth elements.

[0050] A variety of solvents are useful for the treatment of coal-based feedstocks or intermediate coal products (e.g. post-pyrolysis). Polar solvents, hydrogen donating solvents, aliphatic solvents, aromatic solvents, ionic liquid solvents and supercritical fluid extraction (including other solvents) all allow for high flexibility in promoting the production of certain products or product types and changes in solvent systems or processes parameters can account for differences between various coal feedstocks and types. The temperature and pressure of solvent extraction is often tied to the solvent being used, but both subcritical and supercritical solvent extraction may be implemented.

[0051] Multiple solvent extractions with different solvent systems and/or process parameters allows for higher efficiency in converting solid material into more easily processed and potentially more valuable fluid outputs. An example of multiple single stage solvent extractions is provided in FIG. **3**. A feed **201** (which may be a coal-based feedstock, a pyrolysis product or an intermediate that has undergone multiple process steps, including both pyrolysis and solvent extraction) is provided into a first solvent extractor **210**. The solvent extractor **210** uses a specific solvent type, for example, a polar solvent to target certain coal components such as aromatics. The first extract is then split in one or more separation steps **220**, such as a distillation column, resulting in both a light fluid output and a heavy fluid output. Solvent may be recycled back into the solvent extractor **210**. The solids remaining after the solvent extraction **210** are then processed in a second solvent extraction process **211** that uses a different solvent type, for example a hydrogen donating solvent, to extract additional fluids remaining in the solids. Importantly, the order of solvent extraction processes may be reversed or altered to increase the quantity of certain hydrocarbons allowing for diverse product selection. The extract from the second solvent extraction **211** is also fed to a separation step or steps **221**, providing both a light and heavy fluid output and the ability to recycle solvent. Solids remaining after the multistage solvent extraction may be further processed (e.g. pyrolysis or additional solvent extraction) or may be processed as solid products as described herein.

[0052] Multistep solvent extractions, wherein a single solvent is applied multiple times to increase total extraction, and fractionation, wherein a single solvent is applied at different temperatures may also be utilized in some embodiments.

[0053] Solvent extraction experiments were performed to examine the extraction efficiency of tetralin and 1-methylnaphthalene with Cordero Rojo sub-bituminous coal (the same coal as described in Example 2 and Table 1). The experimental procedure was to dry coal for 36 hours at 90° C. under a flowing argon stream; this resulted in coal having <1% (wt) moisture. After drying, the dry coal is weighed and this becomes the basis for the yield calculations below, assuming 0% moisture. Approximately 100 g of coal was placed in a pressure vessel which was then placed in an oven. The desired solvent is pumped at a rate of 0.1 ml/g dry coal per minute and to a pressure above the boiling point at the desired temperature. The oven is turned on and the vessel is heated to a controlled 360° C. The solvent flow continues for 2 hrs after this temperature is reached. Insignificant (assumed zero) gas flows were noted. After 2 hrs, the solvent flow is stopped and the oven turned off, thus allowing the vessel to cool. The pressure drops to atmospheric. After cooling to below the boiling point of the solvent, argon is flowed through the vessel for 36 hrs to remove remaining solvent from the solid residue. The resulting residue is weighed to determine the yield.

[0054] Below are weight-based yield results for dry coal based on the experimental procedure above:

TABLE 2

Weight-based yield results for solvent extraction

Solvent	Tetralin	1-Methyl-Naphthalene	Notes
Solid Residue Yield %	53.3%	71.2%	Residue Weight * 100 Dry Coal Weight
Extract Yield %	46.7%	28.8%	By difference; solvent free basis

Example 4—Integrated Thermochemical Processing

[0055] The solids collected from the pyrolysis (Example 2) and the solvent extraction (Example 3) experiments were then subjected to the second processing option. In other words, solvent extraction solid residue was pyrolyzed and pyrolysis char was solvent extracted. Refer to FIGS. **1**, **2** and **8**.

[0056] The solvent extraction experimental procedure and conditions were the same as described in the Solvent Extraction (Example) except that no drying was required.

[0057] The pyrolysis experimental procedure and conditions were the same as described in the Pyrolysis Example except that no drying was required.

[0058] Below are weight-based tetralin solvent extraction yield results for dry pyrolysis char based on the experimental procedure above:

TABLE 3

Weight-based yield results for pyrolysis followed by solvent extraction

Solvent	Tetralin	Notes
Solid Residue Yield %	97%	Residue Weight * 100 Dry Char Weight
Extract Yield %	3%	By difference; solvent free basis

[0059] Below are weight-based pyrolysis yield results for dry tetralin-based solvent extraction residue based on the experimental procedure above:

TABLE 4

Weight-based yield results for solvent extraction followed by pyrolysis

	Yield %	Notes
Solid Char Yield %	86.1%	Char Weight * 100 Dry Solvent Residue Weight
Tar (liquid) Yield %	5.5%	Cold Trap Liquid Tar Weight * 100 Dry Solvent Residue Weight
Gas Yield %	8.4%	By difference

[0060] Below are the combined 2-step process overall weight-based yield results based on the results above plus results from coal pyrolysis and coal solvent extraction examples. The solvent used was tetralin.

TABLE 5

Weight-based yield results comparison

	Solvent Extraction then Pyrolysis Yield %	Pyrolysis then Solvent Extraction Yield %
Solid Char Yield %	46	77
Tar + Extract (liquid) Yield %	50	13
Gas Yield %	4	10

[0061] It should be noted that in both cases the tar yields from a two-step process is greater than from pyrolysis-only or solvent extraction-only processes.

Example 5—Branching Processes

[0062] By including additional processing steps, including steps after the combination of pyrolysis and solvent extraction produces a highly branched process which can result in a range of products yielded or different specifications and functionality for the same family of product types made. These additional processes convert intermediate products resulting from thermochemical treatment (noted in FIG. **2**). The final product manufacturing processes (formulations) which are fed by intermediates provide high-selectivity an ability to make amounts of product that exhibit performance that ensure economic stability with adjustments to product flows and conditions that permit meeting product-based market demand.

[0063] FIG. **9** provides an example of a highly branched, highly selective process with additional post processing to generate various high-value and useful products. The described process consists of 3 stages which are integrated: thermal and chemical decomposition, vapor-liquid separations, and product manufacture/formulation which can be a single direct process or the production of an intermediate product before further processing to make the high value derivative or end product.

[0064] The thermal and chemical decomposition section consists of a minimum of 2 processing steps, pyrolysis and solvent extraction, with the possible addition of further post treatment steps, which are performed in series. This process provide the maximum liquid intermediate yields (from the separations section) which are the primary feeds to vapor-liquid product manufacturing or formulations. The thermal and chemical decomposition step consists of pyrolysis followed by solvent extraction of the pyrolysis char or of solvent extraction of the primary feedstock followed by pyrolysis of the solvent extraction solid residue. Pyrolysis is the direct or indirect heating of primary feedstock or solvent extraction residue, in a neutral or hydrogen-donor atmosphere (such as hydrogen-rich gas, syngas, or methane). Gas and solid products result from pyrolysis. Solvent extraction consists of contacting the primary feedstock or coal-pyrolysis char which can be multiple steps and with different solvents. Solvents are recovered in the separations section and a solvent-rich stream recycled to solvent extraction. Solvent carried over into the next processing step is minimized. Solvent extraction produces little gas, operates at temperatures below pyrolysis temperatures, and produces a solvent containing extract liquid stream and a solid residue stream. FIG. **8** illustrates the integrated thermal and chemical decomposition step.

[0065] The separations section processes the vapor and liquid intermediates from the thermal and chemical decomposition section to make intermediates which feed for the product formulations section. Depending upon the type of atmosphere in the pyrolysis reactor, gases from the separations section may be processed and recycled to the pyrolysis reactor. A solvent-rich stream will be recovered in the separations section and recycled to the solvent extraction section or used as an intermediate product for further processing into a finished product. The separations section will depend upon both the conversion section (temperature, pressure, processing order, pyrolysis atmosphere, and solvent scheme) and the product formulation sections. Pyrolysis vapors and solvent extraction extract may be combined to feed a single separations section or they may feed separate, parallel separation sections, depending upon which high-value products are deliberately selected and which will be byproducts or co-products. A distillation tower may be the first unit operation in the separations section to remove gaseous products from the thermal and chemical decomposition section and produce various liquid intermediate. Side strippers and side absorbers may be present. The bottoms (residue products) from this first tower will be capable of being sent to a high-vacuum distillation tower to further refine the heaviest material. Depending upon product formulations specifics, the liquid intermediates may be further separated or processed to produce a desired intermediate feed for a specific product formulation. These downstream separations could consist of adsorption, fractionation, crystallization, azeotropic fractionation, extractive distillation, liquid-liquid decanting and extraction, including combinations of these. Unused (for product formulations) intermediates (for example, intermediates with a higher boiling point range) may be recycled to the thermal and chemical decomposition section to further process this material into a more usable intermediates.

[0066] Product formulations consists of two main subsections: intermediate (liquid) and gas product formulations and solids, which are processed in post treatment formulations to make final products. The final formulations will process the intermediates from the separations section to produce 2-10 high-value products and possibly additional lower-value products. Examples of these high-value products can be petrochemicals, carbon fibers, polymers, composites, asphaltenes, binders, coke, and others. Each of these high-value products will be produced in a separate processing unit using a customized feed from the separations section. The solids from the thermal and chemical decomposition section will be sent to solids formulations. Again, several products will be made in separate processing units. Examples of lower value products include water, minerals and clays together with flue gas. Examples of high value product extracts include metals and rare earth elements.

[0067] The processes described herein are somewhat analogous to a crude oil refinery, which is fed crude oil and where there are multiple conversion steps, many separations (especially fractionation) steps, many intermediates produced, and a multitude of derivative products, generally made using distillation as a primary process step to make intermediates followed by discrete hydrocracking, hydrotreating and hydroprocessing to make finished products. However, the described processes herein are specifically tailored for a solid, high carbon content feedstock requiring a distinct and unique integration of thermochemical processes, and which generate a significant volume of solid high value products, liquid products which either technically or economically or both cannot be derived in a petroleum refinery and conversely generates a small volume of fuel products and/or fuel blending components.

[0068] FIGS. **5**-**7** provide more detailed examples of potential process integrations to provide specific examples of high value products. In FIG. **7**, a coal based feed stock in placed into a dryer to remove about 90% of water content. Next, the dried coal is converted in the thermochemical processing step, in this example consisting of two solvent extraction steps and a single pyrolysis step which are fully integrated. The first solvent extraction utilizes a polar solvent (e.g. DMF, ethanol, water) to recover oxygen containing molecules. The second solvent extraction uses a non-polar solvent (e.g. mixed hydrogenated oils, tetralin, supercritical fuels, 1-methyl-naphthalene). Pyrolysis of the solvent extraction residue is performed at 400-1200° F. to produce soil amendment products and building materials together with valuable hydrocarbon containing vapors as intermediates for further processing.

[0069] After thermochemical processing, the various streams are separated by known techniques including, for example, distillation, vacuum distillation, solvent extraction, crystallization, wipe-film evaporation, liquid-liquid extraction and decanting. In some embodiments, products which are separated may be recycled to the thermochemical processing step until a desired composition, conversion or boiling point range has been achieved. In some cases, separations may be performed between thermochemical processing steps (i.e. solvent extraction 1-separations-pyrolysis-solvent extraction 2). For tar streams, vacuum distillation may be used to generate various products based on the boiling point of the stream. Fuel gasses coming off the separations step(s) may be processed in a gas clean up step, such as amine treatments, scrubbing or membrane filtering to remove undesirable gases (e.g. carbon dioxide and SOx and NOx pollutants). After cleaning, fuel gases may also be further converted using dry methane reforming (DMR) or steam methane reforming (SMR) and deployed in the processing steps or sold.

[0070] Solid products from the thermochemical processing steps may be formulated into finished products or used as intermediates from which finished products can be manufactured or sold. Examples products include carbon filler byproduct for building materials, further processing to produce activated-carbon products for environmental management or used to make soil amendments or further calcined to produce coke.

Example 6—Branching from Thermochemical Coal Processing

[0071] With reference to FIGS. **5** and **6** and this Example demonstrates how thermochemical processing of coal can be adapted and is flexible to produce a multitude of distinctive product manufacturing outcomes based upon the unique integrated and synergistic operation of the thermochemical process defined herein. The examples describe laboratory scale experiments that demonstrate proof of concept and viability of additional conversion of coal based materials into high demand and high value products.

Coal Exfoliates

[0072] Described are coal solids from which polar and non-polar molecules have been extracted with highly exfoliated properties and high surface area form, which may be used as soil remediation additives, gas/fluid absorbents, graphene oxide spray slurries, and chars for gasification and hydrogenation.

[0073] Experimentally, a two-step experimental process including: 1) Removal of polar molecules via a continuous extraction using DMF at 140° C. @1 atm and 2) Removal of non-polar molecules via supercritical CO_2 extraction at 40° C. @ 75 atm. The two steps can be applied in any order.

Room Temperature Urethane Foam Composite Synthesis

[0074] Described are organic composite materials consisting of an organic matrix filled with reinforcing particles with sufficient structural strength to act as fillers in skin/matrix structural composites or as freestanding foams for acoustic modulation, thermal insulation, ballistic impact mitigation or buoyancy. These coal based functionalized carbon particles together with a coal derived urethane matrix may produce a low cost polymeric matrix composite (PMC) with highly desirable properties.

[0075] Described herein is a process that produces urethane composites from organic coal extracts without intermediate separation of the extract into its individual chemical or boiling point range constituents, by reacting two solutions at room temperature to form a durable foam with significantly greater volume in a matter of minutes. This process requires no caustic or dangerous reagents during the foam synthesis step and uses the alcoholic/phenolic OH groups on the extract and reacts them in standard fashion with a di-isocyanate cross-linking agents to produce a non-differentiated poly-urethane having good thermal capability as well as reasonable toughness, tensile strength and elasticity. This process also takes advantage of the alcoholic/phenolic OH groups on graphene oxide produced from coal via the Hummer's method or graphitic coal char produced from coal. The addition of graphene oxide or graphitic coal char would greatly increase the strength of the coal PMC.

[0076] Experimentally produced coal extract is made in a continuous Soxhlet process using a standard evaporator, condenser and filter/syphon scheme with dimethylformamide as the solvent. A portion of the coal extract is then pyrolysed at 850° C. for 10-15 minutes in wet air and then crushed to a 200-mesh size. As a laboratory example, graphene oxide is produced via the standard Hummer's method from coal. A mixture of 0.5 g of water and 1% (w/w %) graphene oxide or 1% (w/w %) graphitic coal char, 0.1 g of dibutyltin dilaurate and 2 g of the coal extract is be prepared. Approximately 14 g of toluene d-isocyanate is added to the mixture and stirred by hand vigorously, which causes the solution to foam, after which is allowed to cool to room temperature.

Production of Polyamides from Coal

[0077] Described is a process that produces polyamides from organic coal extracts without intermediate separation of the extract into its individual chemical or boiling point range constituents. This process takes advantage of the carboxylic acid groups on the extract and reacts them in standard fashion with a diamine cross-linking agents to produce a non-differentiated polyamides having good thermal capability as well as reasonable toughness, tensile strength and elasticity.

[0078] Coal extract is made by suspending coal in a high temperature, high pressure tetralin. The dissolved extract precipitates from solution as the temperature and pressure is reduced. As a laboratory scale example, 0.5 g of the solid extract is then dissolved in DMF and heated under reflux at 130° C. for 4 hours with a 0.5 g of hexamethylene diamine. The solution is then placed in a heated petri dish and the DMF evaporated to produce deposits of the polyamide.

[0079] A second sample of polyamide is made by suspending 10 g coal in dimethylformamide at room temperature. This dissolved extract is separated by filtration from the solids and then directly reacted with 0.5 g of hexamethylene diamine at 150° C. and 1 atmosphere pressure. The solution was refluxed for 4 hours and placed in a heated petri dish to form the polyamide deposit as above.

[0080] By varying chemical composition, reaction conditions and solvent systems, engineered polyamides can be produced that have different physical, chemical and intrinsic properties, like flexibility, tensile strength, glass transition temperature of the resulting polymer.

Conductive Composite Derived from Coal

[0081] There is a current technical need for organic composite materials which have sufficient electrical conductivity to shield the electromagnetic emission coming from computer CPU's, cell phones, microwave ovens and the like. High cost thermoplastics filled with moderate cost carbon black is commonly used, but the market is looking for fillers with higher conductivity at lower fill volume. Graphene and multi or single walled carbon nanotubes function perfectly in this role; however, their high price prevents them from achieving widespread use. A coal based carbon particle with a prolate or oblate shape may achieve a lower volume fill in an electrically conductive composite at a significantly lower price.

[0082] Described is a three step process to make an electrically conductive organic composite system consisting of a coal based derived polymeric matrix composite (PMC) that utilizes a coal based polymeric base with a second, coal based, carbon filler to form an electrically conductive composite.

[0083] The process scheme consists of 3 stages, namely **1**) Extraction of organic residue, 2) Conversion of resulting solid to functionalized graphitic char, and 3) Reacting the residue and functionalized char with a di-isocyanate to make a urethane based polymeric composite.

[0084] Experimentally, the coal residue is extracted using DMF as a solvent at temperatures up to 450° C. where temperatures over 150° C. require a pressure vessel with increased volume of extract yield attainable with increasing temperature. This solution is then used in making the composite. The solids remaining after the residue extraction are pyrolysed at 850° C. for 10-15 minutes and the char is then ground to a 200-mesh size and further ground on a ball mill with ethanol added as a carrier fluid. After milling for 16 hours, the char is filtered to remove the solvent and then placed in a stainless steel bomblet with 1/10 equivalent weights of a di-isocyanate. The bomblet is sealed and heated to 400° C. to functionalize the char. The char is then washed with several aliquots of acetone to remove the excess di-isocyanate and dried.

Polyesters Derived from Coal

[0085] Described is a process that produces polyesters from organic coal extracts without intermediate separation of the extract into its individual chemical constituents. This process takes advantage of the carboxylic acid groups on the extract and reacts them in standard fashion with a diol cross-linking agents to produce a non-differentiated polyesters having good thermal capability as well as reasonable toughness, tensile strength and elasticity.

[0086] Coal extract is made by suspending coal in a high temperature, high pressure tetralin. The dissolved extract precipitates from solution as the temperature and pressure are reduced. Experimentally, 0.5 g of the solid extract is dissolved in DMF and heated under reflux at 130° C. for 4 hours with a 0.35 g of ethylene glycol. The solution is then placed in a heated petri dish and the DMF evaporated to produce deposits of the polyester.

[0087] A second sample of urethane is made by suspending 10 g coal in dimethylformamide at room temperature and the extract is separated by filtration from the solids and then directly reacted with 0.35 g of ethylene glycol at 150°

C. and 1 atmosphere pressure. The solution was refluxed for 4 hours and placed in a heated petri dish to form the polyester deposit as above.

[0088] To control desirable properties, substitution of other glycols such as propylene glycol, benzenediol, or bisphenol may result in a similar polymer and that in combination with mixtures of diols can be used to control desirable properties, like flexibility, tensile strength, glass transition temperate, of the resulting polymer.

Structural Foam Composite

[0089] Described is a multi-step process, including: 1) Liquid Extraction of polar organic residue from low rank coals, 2) Distillation or other separation of the polar extract to recover high volatile organics and toluene and other selected aromatics, 3) Conversion of these remaining aromatics to di-isocyanates via acidic nitration followed by hydrogenation, followed by phosgene carboxylation, 4) Conversion of the remaining solid to functionalized graphitic char and 5) Reacting the residue, the di-isocyanate and functionalized char to make a urethane based polymeric composite.

[0090] The coal residue is extracted using DMF as a solvent at temperatures up to 450° C. where temperatures over 150° C. require a pressure vessel and the volume yield of extract increases with temperature. Prior to reacting to form the composite, the concentration of residue in the solvent should approach 1 g residue/2 g solvent. i.e. as close to saturation as possible. This solution is used to make the composite.

[0091] Toluene is nitrated in a HNO_3/H_2SO_4 solution and the di-nitrate hydrogenated to the di-amine with hydrogen at 500° C. in a pressure vessel. The diamine is converted to di-isocyananțe by exposure to phosgene at 250° C.

[0092] The solids remaining after the residue extraction are then pyrolysed at 850° C. for 10-15 minutes in wet air and then crushed to a 200-mesh size. This powder is further ground on a ball mill with ethanol added as a carrier fluid. After milling for 16 hours, the char is filtered to remove the solvent and then placed in a stainless steel bomblet with equal weight of extracted residue and equal (residue+char) weight of the di-isocyanate. The bomblet is sealed and heated to 180° C. to form the composite.

[0093] The resulting foam had a density of 0.33 g/cc and a crush strength>150 PSI.

Urethanes from Coal

[0094] Described is a process that produces urethanes from organic coal extracts without intermediate separation of the extract into its individual chemical constituents. This process reacts alcoholic/phenolic OH groups on the extract a with a di-isocyanate cross-linking agents to produce a non-differentiated polyurethane having good thermal capability as well as reasonable toughness, tensile strength and elasticity.

[0095] Experimentally, coal extract was made by suspending coal in a high temperature, high pressure tetralin solution, whereby the dissolved extract precipitated from solution as the temperature and pressure were reduced. Experimentally, 0.5 g of the solid extract is then dissolved in acetone and heated under reflux at 60° C. for 4 hours with a 0.25 g of toluene di-isocyanate. The solution is then placed in a heated petri dish and the acetone evaporated to produce films of the urethane. A second sample of urethane is made by suspending 10 g coal in dimethylformamide at room temperature. This dissolved the extract is separated by filtration from the solids and then directly reacted with 0.5 g of toluene di-isocyanate at 150° C. and 1 atmosphere pressure. The solution is refluxed for 4 hours and placed in a heated petri dish to form the urethane film as above.

[0096] A third sample is made identically to sample 2 with the exception that 2 drops of di-butyl tin dilaurate is added to the isocyanate mixture as a catalyst and the solution is refluxed for only 1 hour prior to placing in a dish to evaporate the solvent.

[0097] Substitution of other di-isocyanates such as 1,6-diisocyanato hexane may result in a similar polymer and that mixtures of isocyanates can be used to control desirable properties, like flexibility, tensile strength, glass transition temperate, of the resulting polymer.

Graphene/Graphene Oxide Films and Powders Derived from Coal

[0098] Described is a multi-step process for the synthesis of graphene powders and films from coal as well as outlining a pathway to synthesize graphite oxide powders and reduced graphene oxide films from coal. The process includes: 1) Volatile burn off of organic material from coal for 30 minutes at 850° C. and 2) High temperature graphitization in an inert, vacuum environment of resulting solids via induction heating (>2500° C.) of a graphite crucible that contains the resulting solid from step 1.

[0099] The graphene powder or film is then produced by: 3) Tip/bath sonication of resulting material in spray friendly solvents (ethanol and isopropyl alcohol), 4) Centrifugation of the material to select nanoflake material in supernatant followed by decanting of solution to remove the bottom solid material, 5) Vacuum drying of the supernatant produces graphene flake powder (powder synthesis), 6) Forced nebulization of supernatant from step 4 onto heated substrates to form conductive films of variable thickness and conductivities, and 7) Synthesized films were then further annealed via tube furnace annealing from 800-1450° C. (Film synthesis).

[0100] Alternatively, graphite oxide powder and graphene oxide films may be produced via: 3) Oxidation of material using strong oxidizer for variable time or until violent oxidation of solution occurs. The oxidizing solution consisted of 98% sulfuric acid, potassium permanganate, and sodium nitrate, 4) The solids are collected via centrifugation and washed 3× with deionized water with each wash followed by centrifugation and 5) The solution supernatant was discarded and the solids dried via freeze drying (Powder synthesis).

Example 7—Proximate and Ultimate Analysis

[0101] Analysis of Pyrolysis Char

[0102] Sample ID: CE-16-Pc (Char)

TABLE 6

Proximate and Ultimate Analysis of Pyrolysis Char (Refer to Example 2, Table 1)

	As Received wt %	Moisture Free wt %	Moisture & Ash Free wt %	ASTM Method
	Proximate Analysis			
Moisture	1.55	*****	*****	D7582
Ash	11.46	11.64	*****	D7582

TABLE 6-continued

Proximate and Ultimate Analysis of Pyrolysis Char (Refer to Example 2, Table 1)

Volatile Matter	24.98	25.37	28.71	D7582
Fixed Carbon	62.02	62.99	71.29	calculated
Total	100.00	100.00	100.00	
	Ultimate Analysis			
Moisture	1.55	*****	*****	D7582
Ash	11.46	11.64	*****	D7582
Carbon	73.89	75.05	84.93	D5373
Hydrogen	3.34	3.39	3.83	D5373
Nitrogen	3.87	3.93	4.45	D5373
Sulfur	0.45	0.46	0.52	D4239
Oxygen	5.45	5.53	6.26	calculated
Total	100.00	100.00	100.00	

	As Received Btu/lb	Moisture Free Btu/lb	Moisture & Ash Free Btu/lb	ASTM Method
Heating Value	12,237	12,430	14,067	D5865

[0103] Hydrogen and Oxygen values reported do not include hydrogen and oxygen in the free moisture associated with sample. Reported results calculated by ASTM D3180. Results are an average of 2 runs.

Analysis of Pyrolysis Char Form the Pyrolyzed Residue of the Solvent Extracted Coal

[0104] Sample ID: CE-13-Res-Pc (Char)

TABLE 7

Proximate and Ultimate Analysis of Pyrolysis Char where pyrolysis occurred post solvent extraction (Refer to Example 4, Table 4)

	As Received wt %	Moisture Free wt %	Moisture & Ash Free wt %	ASTM Method
	Proximate Analysis			
Moisture	1.07	*****	*****	D7582
Ash	13.22	13.36	*****	D7582
Volatile Matter	25.59	25.87	29.86	D7582
Fixed Carbon	60.11	60.77	70.14	calculated
Total	100.00	100.00	100.00	
	Ultimate Analysis			
Moisture	1.07	*****	*****	D7582
Ash	13.22	13.36	*****	D7582
Carbon	70.81	71.58	82.63	D5373
Hydrogen	3.41	3.45	3.98	D5373
Nitrogen	1.27	1.29	1.49	D5373
Sulfur	0.21	0.21	0.24	D4239
Oxygen	10.00	10.11	11.67	calculated
Total	100.00	100.00	100.00	

	As Received Btu/lb	Moisture Free Btu/lb	Moisture & Ash Free Btu/lb	ASTM Method
Heating Value	11,549	11,674	13,475	D5865

[0105] Hydrogen and Oxygen values reported do not include hydrogen and oxygen in the free moisture associated with sample. Reported results calculated by ASTM D3180. Results are an average of 2 runs.

Analysis of Residue from the Solvent Extraction of the Pyrolysis Char Tested in Table 6

[0106] Sample ID: CE-16-Res

TABLE 8

Proximate and Ultimate Analysis of solvent extraction residue of the sample (CE-16-Res) tested in Table 6 (Refer to Example 4, Table 3)

	As Received wt %	Moisture Free wt %	Moisture & Ash Free wt %	ASTM Method
	Proximate Analysis			
Moisture	0.50	*****	*****	D7582
Ash	10.11	10.16	*****	D7582
Volatile Matter	23.59	23.70	26.38	D7582
Fixed Carbon	65.81	66.14	73.62	calculated
Total	100.00	100.00	100.00	
	Ultimate Analysis			
Moisture	0.50	*****	*****	D7582
Ash	10.11	10.16	*****	D7582
Carbon	75.25	75.63	84.18	D5373
Hydrogen	3.69	3.71	4.13	D5373
Nitrogen	1.41	1.41	1.57	D5373
Sulfur	0.34	0.34	0.38	D4239
Oxygen	8.71	8.75	9.74	calculated
Total	100.00	100.00	100.00	

	As Received Btu/lb	Moisture Free Btu/lb	Moisture & Ash Free Btu/lb	ASTM Method
Heating Value	12,572	12,635	14,063	D5865

[0107] Hydrogen and Oxygen values reported do not include hydrogen and oxygen in the free moisture associated with sample. Reported results calculated by ASTM D3180. Results are an average of 2 runs.

TABLE 9

Quality Control

Parameter	Reference Material	Expected	Result	% Recovery
Ash	AR2775	6.80	6.32	93
Volatile Matter	AR2775	37.77	39.6	105
Carbon	hs-10006a	65.6	63.64	97
Hydrogen	hs-10006a	6.69	6.72	100
Nitrogen	hs-10006a	8.2	8.45	103
Sulfur	AR1701	0.53	0.55	104
Heating Value, Btu/lb	Benz 1	11,373	11,413	100

STATEMENTS REGARDING INCORPORATION BY REFERENCE AND VARIATIONS

[0108] All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

[0109] The use of the terms "a" and "an" and "the" and "at least one" and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The use of the term "at least one" followed by a list of one or more items (for example, "at least one of A and B") is to be construed to mean one item selected from the listed items (A or B) or any combination of two or more of the listed items (A and B), unless otherwise indicated herein or clearly contradicted by context. The terms "comprising," "having," "including," and "containing" are to be construed as open-ended terms (i.e., meaning "including, but not limited to,") unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., "such as") provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

[0110] Preferred embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Variations of those preferred embodiments may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.

[0111] All references throughout this application, for example patent documents including issued or granted patents or equivalents; patent application publications; and non-patent literature documents or other source material; are hereby incorporated by reference herein in their entireties, as though individually incorporated by reference, to the extent each reference is at least partially not inconsistent with the disclosure in this application (for example, a reference that is partially inconsistent is incorporated by reference except for the partially inconsistent portion of the reference).

[0112] The terms and expressions which have been employed herein are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments, exemplary embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims. The specific embodiments provided herein are examples of useful embodiments of the present invention and it will be apparent to one skilled in the art that the present invention may be carried out using a large number of variations of the devices, device components, methods steps set forth in the present description. As will be obvious to one of skill in the art, methods and devices useful for the present methods can include a large number of optional composition and processing elements and steps.

[0113] When a group of substituents is disclosed herein, it is understood that all individual members of that group and all subgroups, including any isomers, are disclosed separately. When a Markush group or other grouping is used herein, all individual members of the group and all combinations and subcombinations possible of the group are intended to be individually included in the disclosure. When a compound is described herein such that a particular isomer of the compound is not specified, for example, in a formula or in a chemical name, that description is intended to include each isomers of the compound described individual or in any combination. Additionally, unless otherwise specified, all isotopic variants of compounds disclosed herein are intended to be encompassed by the disclosure. For example, it will be understood that any one or more hydrogens in a molecule disclosed can be replaced with deuterium or tritium. Isotopic variants of a molecule are generally useful as standards in assays for the molecule and in chemical and biological research related to the molecule or its use. Methods for making such isotopic variants are known in the art. Specific names of compounds are intended to be exemplary, as it is known that one of ordinary skill in the art can name the same compounds differently.

[0114] Many of the molecules disclosed herein contain one or more ionizable groups [groups from which a proton can be removed (e.g., —COOH) or added (e.g., amines) or which can be quaternized (e.g., amines)]. All possible ionic forms of such molecules and salts thereof are intended to be included individually in the disclosure herein. With regard to salts of the compounds herein, one of ordinary skill in the art can select from among a wide variety of available counterions those that are appropriate for preparation of salts of this invention for a given application. In specific applications, the selection of a given anion or cation for preparation of a salt may result in increased or decreased solubility of that salt.

[0115] Every formulation or combination of components described or exemplified herein can be used to practice the invention, unless otherwise stated.

[0116] Whenever a range is given in the specification, for example, a temperature range, a pressure range, a time range or a composition or concentration range, all intermediate ranges and subranges, as well as all individual values included in the ranges given are intended to be included in the disclosure. It will be understood that any subranges or individual values in a range or subrange that are included in the description herein can be excluded from the claims herein.

[0117] All patents and publications mentioned in the specification are indicative of the levels of skill of those skilled in the art to which the invention pertains. References cited herein are incorporated by reference herein in their entirety to indicate the state of the art as of their publication or filing date and it is intended that this information can be employed herein, if needed, to exclude specific embodiments that are in the prior art. For example, when composition of matter are claimed, it should be understood that compounds known and available in the art prior to Applicant's invention, including compounds for which an enabling disclosure is provided in the references cited herein, are not intended to be included in the composition of matter claims herein.

[0118] As used herein, "comprising" is synonymous with "including," "containing," or "characterized by," and is inclusive or open-ended and does not exclude additional, unrecited elements or method steps. As used herein, "consisting of" excludes any element, step, or ingredient not specified in the claim element. As used herein, "consisting essentially of" does not exclude materials or steps that do not materially affect the basic and novel characteristics of the claim. In each instance herein any of the terms "comprising", "consisting essentially of" and "consisting of" may be replaced with either of the other two terms. The invention illustratively described herein suitably may be practiced in the absence of any element or elements, limitation or limitations which is not specifically disclosed herein.

[0119] One of ordinary skill in the art will appreciate that starting materials, biological materials, reagents, synthetic methods, purification methods, analytical methods, assay methods, and biological methods other than those specifically exemplified can be employed in the practice of the invention without resort to undue experimentation. All art-known functional equivalents, of any such materials and methods are intended to be included in this invention. The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention that in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims.

We claim:

1. A method for converting coal into a plurality of high value coal products and extracts comprising:

providing a feedstock, wherein said feedstock is at least partially derived from coal;

processing said feedstock, wherein said processing step includes a combination of pyrolysis and solvent extraction,

wherein said pyrolysis and solvent extraction are integrated and carried out under conditions for generating a plurality of high value coal products.

2. The method of claim **1**, wherein greater than or equal to 50% by mass dry basis of said high value coal products are liquid at standard temperature and pressure.

3. The method of claim **1** or **2**, wherein said step of processing said step is highly branched and highly selective.

4. The method of any of claims **1-3**, wherein said pyrolysis is performed at a pressure selected from the range of 0.5 atm to 15 atm.

5. The method of any of claims **1-4**, wherein said pyrolysis is performed at a temperature selected from the range of 400° C. to 1200° C.

6. The method of any of claims **1-5**, wherein said pyrolysis is performed in less than or equal to 5 seconds.

7. The method of any of claims **1-6**, wherein said pyrolysis is integrated with said solvent extraction.

8. The method of any of claims **1-7**, wherein said pyrolysis generates a mass percentage of gas of less than or equal to 25%, excluding water vapor.

9. The method of any of claims **1-8**, wherein said pyrolysis is performed in the presence of hydrogen gas, methane, syngas or any combination thereof.

10. The method of any of claims **1-9**, wherein said pyrolysis is flash pyrolysis.

11. The method of any of claims **1-10**, wherein said solvent extraction is performed with at least one liquid solvent.

12. The method of any of claims **1-11**, wherein said at least one solvent is selected from the group consisting of an aliphatic solvent, an aromatic solvent, a polar solvent, a hydrogen donating solvent, an ionic liquid solvent and any combination thereof.

13. The method of any of claims **1-12**, wherein said solvent extraction is performed with at least two liquid solvents.

14. The method of claim **13**, wherein a first solvent is a polar solvent and a second solvent is a hydrogen donating solvent or vice versa.

15. The method of any of claims **1-14**, wherein said solvent extraction is a single stage solvent extraction, multiple single stage solvent extractions, a single multistage solvent extraction, multiple multistage solvent extractions or a combination of single stage and multistage solvent extractions.

16. The method of any of claims **11-15**, wherein said solvent extraction is performed at a temperature less than the critical temperature of said at least one solvent.

17. The method of any of claims **1-16**, wherein said solvent extraction is performed at less than or equal to 350° C.

18. The method of any of claims **1-17**, wherein said solvent extraction generates a mass percentage of gas less than or equal to 5%, excluding water vapor.

19. The method of any of claims **11-18**, wherein one of said at least one solvents comprises tetralin (1,2,3,4-Tetrahydronaphthalene), 1-methyl-napthalene, toluene, dimethylformamide (DMF) or any combination thereof.

20. The method of any of claims **1-19**, wherein said solvent extraction is performed upstream of said pyrolysis.

21. The method of any of claims **1-20**, wherein said pyrolysis is performed upstream of said solvent extraction.

22. The method of any of claims **1-21**, wherein a portion of products for said pyrolysis step are recycled to said solvent extraction.

23. The method of claim **22**, wherein said processing step comprises multiple solvent extractions and products from a later solvent extraction are recycled to an earlier solvent extraction or said pyrolysis or used as an intermediate for upstream further processing.

24. The method of any of claims **1-23**, wherein said feedstock at least partially derived from coal is greater than or equal to 90% unrefined coal by weight.

25. The method of claim **24**, wherein said unrefined coal is physically, chemically or thermally preprocessed prior to said step of processing.

26. The method of any of claims **1-25**, wherein a portion of said feedstock is one or more product streams from said pyrolysis, said solvent extraction, recycle streams or a combination thereof.

27. The method of any of claims **1-26**, wherein said feedstock at least partially derived from coal comprises subbituminous coal.

28. The method of any of claims **1-27**, wherein said feedstock is at least partially derived from coal is derived from run of mine coal.

29. The method of any of claims **1-28**, wherein said high value coal products comprise less than or equal to 10% fuel products.

30. The method of any of claims **1-29**, wherein said high value coal products comprise polymers or polymer precursors.

31. The method of any of claims **1-30**, where said high value coal products comprise polyurethane.

32. The method of any of claims **1-31**, wherein said high value coal products comprise composite polyurethane foam.

33. The method of any of claims **1-32**, wherein said high value coal products comprise polyamides.

34. The method of any of claims **1-33**, wherein said high value coal products comprise polyesters.

35. The method of any of claims **1-34**, wherein said high value coal products comprise adhesives.

36. The method of any of claims **1-35**, wherein said high value coal products comprise aromatics.

37. The method of claim **36**, wherein said high value coal products comprise benzene, toluene, xylene, phenols, cresols, xylenols, naphthenols, C9 single aromatic rings, C10 single aromatic ring isomers or any combination thereof.

38. The method of any of claims **1-37**, wherein said high value coal products comprise paraffins, olefins or a combination thereof.

39. The method of any of claims **1-38**, wherein said high value coal products comprise asphaltenes.

40. The method of any of claims **1-39**, wherein said high value coal products comprise coal tar, distillates, pitch, carbon fibers or any combination thereof.

41. The method of any of claims **1-40**, wherein said high value coal products comprise soil amendments

42. The method of any of claims **1-41**, wherein said high value coal products comprise building materials.

43. The method of any of claims **1-42**, wherein a significant portion of said high value coal products are solids.

44. The method of claim **43**, wherein said solids can be converted to construction materials, composite materials, liquid additives or any combination thereof when combined a resin, liquid or other bi-product generated by the methods described in claims **1-43**.

45. The method of claim **44**, wherein said extracts can include metals and rare earth elements.

46. A method for converting coal into a plurality of high value coal products comprising:

providing a primary feedstock at least partially derived from coal;

processing said primary feedstock, wherein said processing sequence is:

a pyrolysis step, wherein said pyrolysis step is performed in less than or equal to 10 seconds performed in a hydrogen rich atmosphere; and

a solvent extraction step, wherein said solvent extraction step is performed with at least one liquid solvent, wherein said liquid solvent is selected from the group consisting of: a polar solvent, a hydrogen donating solvent and any combination thereof;

wherein said pyrolysis step is the first processes step performed on said primary feedstock and said solvent extraction step is the second process step carried out on a solid char produced from said pyrolysis step; and

wherein said pyrolysis step and said solvent extraction step are integrated and carried out under conditions for generating a plurality of high value coal products.

47. The method of claim **46**, wherein said pyrolysis step is a flash pyrolysis process.

48. The method of claim **46** or **47**, wherein said solvent step process is a single stage solvent extraction, multiple single stage solvent extractions, a single multistage solvent extraction, multiple multistage solvent extractions or a combination of single stage and multistage solvent extractions.

49. The method of any of claims **46-48** wherein said solvent extraction step uses two or more solvents.

50. The method of any of claims **46-49**, wherein processing said feedstock further comprises one or more separation steps occurring after said pyrolysis step, after said solvent extraction step or in between multiple solvent extractions.

* * * * *