

REVIEW

THE EFFECTS OF IMPREGNATION OF COAL BY ALKALI SALTS UPON CARBONIZATION PROPERTIES

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ABSTRACT

The co-carbonization of coking and caking coals with potassium and sodium salts destroys the coking and caking capacities of the coals. Further, the resultant char is of high surface area and exhibits a high chemical reactivity to oxidizing gases because of the catalytic influence of potassium retained within the char.

This article attempts to explain the above phenomena, i.e. the loss of coking mechanisms, the development of high surface areas and the retention of the potassium. Initially, current theories are outlined of coking mechanisms which establish the anisotropic, carbonaceous structural units within resultant cokes. These structural units are best observed as isochromatic areas in colours of blue, yellow or purple, using a polarized light microscope and a half-wave retarder plate in conjunction with polished surfaces of coke. When a coking coal is carbonized, it first softens and melts to form an isotropic, pitch-like fluid. On further heating, anisotropic units of irregular shape develop from within this fluid phase. In coal systems, these units grow to about 0.5–5.0 μm at which stage they join or fuse together but do not coalesce. Their identity is maintained, and they establish what are termed fine-mosaics. At the same time, the macro-properties of coke, e.g. porosity, are established.

The formation of these anisotropic mosaics occurs via the growth of lamellar nematic liquid crystals containing stacked lamellar molecules. The liquid crystals possess the crystalline order which is transferred to the solid coke substance. It is the plasticity of the liquid crystals which allows the growing anisotropic units to fuse together, and the introduction of disclinations which impart desirable properties to the coke substance.

The addition of potassium salts to coking coals is thought to reduce the fluidity of the coals primarily by increasing the number of cross-links which normally exists between the aromatic and hydroaromatic constituent molecules (building blocks) in the coal. Such an increase results, in turn, in an increase in molecular weight of the coal, decrease in its fluidity upon heat treatment, and the consequent decrease in mobility of planar regimes preventing their alignment to form the liquid crystals and then the anisotropic mosaics. It is suggested that the presence of potassium results in a higher oxygen content being present in the coal upon heating, either by reducing the rate of oxygen evolution from the coal as CO, CO₂, and/or water or by acting as an intermediate to extract additional oxygen from the steam added as a reactant to the system (that is, steam gasification). Thus, an increased oxygen content results in more cross-linking in the structure probably via ether linkages between aromatic and/or hydroaromatic regimes. This increase in cross-linkage creates the

isotropic carbon of the char, the spaces between the cross-linked constituent molecules being microporosity responsible for the high surface area of the char. The potassium could be retained within the microporosity by being bonded to the oxygen attached to the carbon.

INTRODUCTION

Gasoline from coal

The decline in the availability of fuels derived from petroleum (in particular the linear hydrocarbons used in the internal combustion engine) has accelerated a major research effort into the chemistry and technology of fuels derived from coal. The major problem here is the conversion of the complex coal molecular systems into smaller units more ideally suited for the chemical industry and the internal combustion engine.

Mills [1] presents a succinct and hard-thinking over-view of the several processes being examined today for conversions from coal to more amenable products. Currently, for fuels for the internal combustion engine, it would appear to be economically more attractive to break-down the molecular systems in raw coal rather drastically into carbon monoxide and methane rather than attempt partial hydrogenation of solvent refined coals into smaller molecular systems, still based on molecular configurations in coal.

All gasification processes of coal produce carbon monoxide and hydrogen. These are readily converted to methanol. Mobil researches [2], using a new class of molecular sieve as catalyst now claim to be able to convert, almost quantitatively, methanol to gasoline, of adequate octane number, and water.

Steam gasification of coal char can produce a mixture of methane, carbon dioxide, hydrogen and carbon monoxide. An attractive route would therefore be the separation of such a mixture of gases, the methane being used as pipeline gas and the hydrogen and carbon monoxide being converted to methanol and then to liquid fuels suitable for transportation needs. However, a major problem has been the high temperatures needed for steam gasifications (1800°F, 985°C, 1256 K) this requirement necessitating complicated and expensive equipment.

However, according to Mills [1] experiments sponsored by ERDA and carried out at the Pittsburgh Energy Research Center, Exxon, Battelle and TRW show that certain alkaline catalysts — notably sodium and especially potassium oxide — greatly speed up the coal—steam reaction. Addition of 15 atom % of potassium increases the reaction rate by ten-fold. A major benefit of this catalysis is the ability to operate at lower temperatures where the methane content of the product gases is increased because of thermodynamic considerations. The use of lower temperatures also significantly reduces the demands on material specifications and operating costs.

The alkali oxide is sufficiently volatile to be mobile and can be re-cycled with the coal. Work at Battelle is directed to making the sodium or potassium more effective by “cooking” the coal with the alkali solution. This not only

increases the coal's effective surface area but also eliminates its propensity to cake. Thus, the addition of sodium or potassium (presumably as hydroxide) introduces a triple function into coal gasification:

(i) It prevents a coking or caking process whereby the gasifier becomes inoperable because of loss of mobility of char (coke) and of a reduction in the permeability (ventilation) of the steam and its carrier.

(ii) As well as destroying the tendency of the coal to cake or coke it apparently increases the internal surface area of the resultant char. Thus, the interface between the char and the steam is considerably extended, this making a most valuable contribution to this heterogeneous type of reaction.

(iii) The sodium and potassium, in their own right, are acting as gasification catalysts, so enhancing the rate of production of methane, carbon monoxide and hydrogen at a given temperature, or reducing the temperature for a given reaction rate (always economically attractive).

COKING AND OPTICAL TEXTURE

Optical texture

According to Mills [1], the co-carbonization of alkali metal hydroxides (alkali oxides) with coal substance destroys the propensity of the coal to coke or cake and enhances the internal surface area of the resultant char. These two effects are probably closely inter-related and are both the consequence of the interaction of the alkali metal oxides, or derivatives, with coal substance.

Initially, let us summarize the caking or coking process in fairly general physical terms to establish basic guidelines. We will not be too concerned with the detail of the chemical transformations. For a coal to cake or coke during pyrolysis requires that the coal substance becomes fluid, usually between 400° and 500°C. The fluidity of coal (measured for example by a Gieseler plastometer) increases with rank of the coal from high-volatile to medium-volatile type of bituminous coal. The creation of fluidity results from both the depolymerization of coal substance by the thermal treatment and the general effect of increase of fluidity with increasing temperature as found for pitch-like substances. Fluidity increases with heat-treatment temperature to a maximum somewhere in the region of 500°C. On heating the coal pyrolysis system to temperatures beyond this maximum, the fluidity decreases rather sharply as a re-polymerization process develops which leads ultimately to semi-coke, or char, dependent upon the rank of the coal being examined. It is this re-polymerization stage which is critical to the coking process.

Examination of the semi-coke, of polished surfaces, using polarized light optical microscopy reveals various types of optical texture [3-5]. With semi-cokes from the high-volatile caking coals such an examination reveals an optical texture which is essentially isotropic, but in which can be detected small-sized (< 1.0 μm) anisotropic units of structure. With increasing rank of coal, to that of the prime-coking (metallurgical) coals, the size of these

anisotropic units of structure also increases. In semi-cokes from the prime coking coals the optical texture is (apart from inorganic and non-fusing organic petrographic components) essentially and continuously anisotropic. The anisotropic units are classified according to size and shape [4,5] ranging from mozaics (0.2–2 μm) to flow-type structures.

The basic cause of the variation in optical texture in semi-cokes from coals of increasing rank is associated directly with the chemical reactivity of the constituent coal molecules (this decreasing with increasing coal rank) and the associated and dependent fluidity of the carbonizing system.

The variations in optical textures of semi-cokes from coals of increasing coal rank can be understood in the same terms as are used to distinguish and understand the optical textures of semi-cokes made from pitch substances based on coal and petroleum as well as single organic compounds [6,7].

Origins of optical texture

The mechanism for the creation of the smaller anisotropic structures in semi-cokes from coal substance is the same mechanism which leads to the formation of the larger anisotropic structures arising during the carbonization of the pitch substances. It is a matter of degree. Or, it is the resultant balance of five principal parameters operating within the system, i.e. reaction temperature, chemical reactivity, fluidity, a "solvent" fraction and extent of re-polymerization. The similarity between pitch and coal systems can be commented upon in terms of e.g. hardness and optical texture if one compares the optical properties of "shot-coke" from a delayed coker with those of a metallurgical coke. Both contain mozaics of about 1 μm diameter.

With a coal-tar pitch or aromatic petroleum-based pitch feedstock, we observe (via optical microscopy) during pyrolysis the growth of *anisotropic* units from within the fluid isotropic pitch. For such starting material these growth units are usually spherical in shape. There is nothing particularly fundamental about this spherical shape although it is indicative of the physical condition of the system. The spherical shape results from the usual dictate of minimum surface area at the interface of a bi-phase system. These spheres are rather viscous and are certainly not solid. Consequently, on contact, following growth, these spheres can coalesce into larger spheres or into other shapes. Eventually, with duration of the heating process (isothermal studies) or with increasing temperature of pyrolysis the anisotropic structures so established become solid as the semi-coke is formed. Coal substances do not pyrolyse to form these spherical units but others more irregular in shape (see below for a further discussion).

Structure within the optical texture

That these spherical growth units are strongly anisotropic as seen by polarized light reflected from polished surfaces is indicative that the molecules within

these spheres are *not* randomly arranged but are stacked essentially parallel to each other [6]. The ordering within the growth units is established by a rather unusual process, that of formation of lamellar nematic liquid crystals (the plastic or viscous anisotropic phase is usually called mesophase). These lamellar, nematic liquid crystals are composed of large, essentially lamellar aromatic molecules.

The conditions necessary for the formation of this liquid crystal phase are rather critical. Initially, the chemical reactivity of the molecular constituents of the material being pyrolyzed must not be too high. If, at relatively low temperatures, this inter-molecular reactivity is too high, then during the initial stages of the carbonization the molecules react with each other, condense or polymerise, to establish a system of increasing viscosity, of increasing average molecular size, of non-planarity of molecules and of three-dimensional cross-linkage, none of which are conducive to mesophase formation. On further heat-treatment these materials lose small-sized molecules as volatile matter to create an isotropic, usually porous, non-graphitizing carbon. If the chemical reactivity is not too high, then polymerization processes are restrained to higher temperatures of pyrolysis. Here, the fluidity of the system is much higher, non-reacting molecules act as a solvent and the larger molecules are capable of movement and orientation to establish the ordered, nematic liquid crystals. Consequently, the molecules forming the liquid crystals have time to grow and do not exhibit random polymerization which establishes the isotropic disordered system. However, once within the liquid crystals the lamellar molecules still undergo polymerization reactions to consolidate and perfect the anisotropy established (probably physical processes initially), within the anisotropic growth units.

Above, we mentioned two extreme types of carbonization systems. One, because of high initial chemical reactivities, leads to the formation of a porous, low density, high surface area, isotropic, non-graphitizing carbon. The second system is that which leads to anisotropic carbon, of large growth units as seen in the optical microscope (large domains in the optical textures). However, restrained chemical reactivity and high fluidity within the systems leads to a non-porous, high density, low surface area, anisotropic graphitizing carbon. Carbonization studies of many systems, including coal-tar pitch, solvent refined coals, coal pitch derived from high pressure gasification systems, as well as petroleum pitches and residues from the many sources provided by the petroleum industry and including model organic compounds, indicate that semi-cokes (or carbons) can be prepared with optical textures in the entire range of size from totally isotropic (no anisotropic growth unit) through small mozaics ($< 0.1 \mu\text{m}$ growth units) to the domains and flow-type anisotropy (10–300 μm in size). The optical textures are the result of variations in the ultimate interactions of temperature, fluidity, reactivity and solvent-power.

COAL CARBONIZATION

Rank and optical texture

The carbonizations of coals of increasing rank are very interesting from this point of view in that, within this one type of parent substance (i.e. coals) a complete range of optical textures can be created in resultant semi-cokes as one goes from the carbonization of high-volatile, weakly-coking coals to the semi-anthracites and anthracites.

Metallurgical cokes owe their rather unusual (but very useful) properties to a combination of several events. They are formed from these higher rank coals which tend to be relatively high in aromatic content [8]. This creates the possibility of mesophase formation. The chemical reactivity is such that the polymeric processes occur in the temperature zone of maximum fluidity. For these coals the fluidity is lower than in lower rank coals [8] and this lower fluidity prevents significant formation of flow-type anisotropy. Hence, in the pore wall material (of significant thickness because of diminished volatile evolution) are found the mozaic anisotropy and small flow-type anisotropy. The overall properties of cokes in terms of strength and resistance to oxidation and thermal shock are attributable to this unique combination of mozaics, flow-type anisotropy and isotropic material.

Metallurgical coking coal

Because these coal-derived molecules (in fluid coal) are dissimilar, structurally, to those in coal-tar or petroleum pitch (it is difficult to be precise about relative chemical reactivities) and are perhaps somewhat larger in a less fluid system, these metallurgical coals do not form large (e.g. 30 μm) anisotropic growth spheres of low viscosity, but rather smaller growth units (0.2–2 μm) which do not coalesce. Smallness in size (of irregular shape) implies a high viscosity in the mesophase, attributable to both large molecular size and chemical reactivity. Growth implies a constant facility to "take-in" new molecules and to adjust in shape accordingly. With too high a viscosity, this adjustment is not possible. However, these small growth units, on fusing, bond together quite tenaciously (how is not yet understood). Consequently, because of this relatively high viscosity (compared to pitch systems) the volatile emission from the carbonizing system is capable of creating only a limited porosity in macro-pores some hundreds of micrometres in size, as distinct from a sponge (frothy) coke. This limited porosity establishes a suitable density for blast furnace operations. (The coke "dilutes" the iron ore so facilitating the heterogeneous reduction process by carbon monoxide.) This suitable balance of weight of coke, of iron ore and of total volume facilitates the requisite gas flow upwards through the blast furnace.

At the same time, the bonding together of the small growth units of anisotropic carbon is such that the coke substance is extremely strong and is capable

of withstanding the crushing pressure of the overburden in the blast furnace. (That is, when coke-making practice is as to specification.) Also, the fact that the coke is essentially anisotropic and non-porous reduces the chemical reactivity of the coke to carbon dioxide to acceptable levels. Cokes made from coal-tar and petroleum pitch are of relatively low mechanical strength because the larger "crystallite" domains and flow-type anisotropy establish large and often interconnecting porosities which are convenient channels for crack propagation.

Thus, in summary, metallurgical coke has rather unique properties in terms of shape, size and extent of macroporosity, of strength and chemical reactivity, these being established because coking coal substance can form nematic crystals which lead directly to anisotropic structures within coke substance (cell wall material).

Coals of lower rank are formed into semi-cokes which have a smaller optical texture [3,4] and more isotropic carbon because these lower rank coals are less rich in aromaticity and possess more reactive hydrogen and oxygen groupings this leading to "premature" condensations or coke (char) formation.

MODIFICATION OF OPTICAL TEXTURE

Reduction in size of optical texture

Any modification of a carbonization process of a coal which results in the loss of coking properties and presumably a loss also of an anisotropic optical texture must interfere with this process of formation of lamellar nematic liquid crystals from within the isotropic fluid phase of the carbonization process.

Experimental studies and surveys of industrial operations all indicate that it is quite easy to modify the carbonization behaviour of materials which would normally give semi-cokes possessing large domains or flow-type anisotropy in such a way as to *decrease* the size of anisotropic growth units of the optical texture. It is a very difficult exercise to consider how the carbonization process can be modified for a material which would normally give a semi-coke possessing small mosaics in such a way as to *increase* the size of these small growth units of the optical texture. It is an objective of the petroleum industry to up-grade this pitch-like residual material to produce needle-coke material with large flow-type anisotropic growth units. It would appear that it is an objective of the ERDA sponsored research groups [1] to degrade the carbonization of bituminous coals to produce essentially isotropic porous carbons (chars).

Loss of coking properties

Considerable experience is already available to assist with the understanding of mechanisms of loss of coking properties in bituminous coals. In general terms (of not specifically identical but of related chemistry) the same mechanisms are operative when pitches are modified to *reduce* the size of the anisotropic growth units of the optical textures of their cokes.

It is well established that medium-volatile bituminous coals lose their coking capacity by mild oxidation [8]. Studies by Ignasiak et al. [9,10] indicate that extremely small quantities of oxygen (almost beyond the limits of quantitative analysis) are effective in reducing the coking capacity of coals. Goodarzi et al. [11] and Marsh and Goodarzi [12] studied, in particular, the loss of anisotropy via the formation of lamellar nematic liquid crystals in semi-cokes from two vitrinites following pre-oxidation of the vitrinites. Carbonization of these pre-oxidized vitrinites (9 days in air at 373 K) under hydraulic pressures of about 30 MPa did however (unexpectedly) result in anisotropic coke formation with larger domains and much higher optical reflectance than found in cokes from fresh samples of vitrinites (non-oxidized). Here then, are two approaches to produce anisotropic coke and the analysis of these processes helps towards a better understanding of the effects created by chemisorption of molecular oxygen.

The pressurized carbonization would appear to indicate that the oxidation process results in cross-linkage of the "polymeric coal molecule system" of the vitrinite. (This is, of course, not a new concept but its application here is rather interesting.) The original vitrinite possesses an inherent anisotropy associated with its geological origins. The oxidation treatment at 373 K "pins" this inherent anisotropy into a stronger polymeric system. Now, on carbonization *at atmospheric pressure* it is found that the mozaic units in the resultant cokes become smaller with progressive oxidation until only a non-caking isotropic carbon (char) results. This is a consequence of increased molecular size (decreased diffusivity or mobility) of "oxygen-bridged" molecules, the effect being compounded by the associated decrease in fluidity of the system until eventually the system is so cross-linked that dissociation is not possible. The skeletal structure withstands the effects of temperature but loss of volatiles and subsequent distortion of the skeletal structure creates the isotropic, non-fusing char. However, when carbonized under *hydraulic pressure* this inherent anisotropy is maintained and perfected considerably because evolution of volatiles is prevented by the applied pressure such that little significant distortion is introduced into the skeletal structure.

Therefore, the major cause for loss of ability of pre-oxidized coals to form anisotropic coke on carbonization is the loss of mobility of constituent molecules (by oxygen cross-linkage) in the early stages of carbonization. This cross-linkage (ether groupings) of constituent molecules is evidently strong enough to prevent the thermal dissociation of the established skeletal polymeric systems.

Anisotropic to isotropic carbon

It is convenient (and reasonably accurate) to consider isotropic carbons as being three-dimensional, randomly arranged (with limited clustering of layers only) systems. All conversions of carbonizing material from giving anisotropic and graphitizing carbons to giving isotropic and non-graphitizing carbons must

include a mechanism for the establishment of a stable, random polymeric system during the early stages of carbonization. This can be brought about by both chemical and physical methods. It is probable that the co-carbonization of coal and alkali metal salts to produce a porous carbon incorporates both mechanisms.

In fundamental studies of the chemistry of carbonization of model organic compounds, Mochida et al. [13] for anthracene and pyrene found that isotropic carbon, in high yield, resulted from the co-carbonization of each aromatic hydrocarbon with alkali metals, either lithium or sodium or potassium. The type of carbon produced was independent of the alkali metal, starting materials and heating rates. The isotropic carbons had properties, i.e. surface area, crystallite size and specific gravity, comparable to glassy carbons. These isotropic carbons resulted because the metals act as dehydrogenation catalysts, stripping off hydrogen from the anthracene at a relatively low temperature (no fluidity) the resultant anthryl radicals linking up in a quite random way.

Oi et al. [14,15] studied the influence of metal additives to a coal-tar pitch and cracked oil upon the resultant optical textures of cokes so prepared. As found by Marsh et al. [16], for anthracene, the addition of iron (as ferrocene) reduced the unit size of the optical textures in the cokes of Oi et al. from coal-tar pitch. Additions of 1200 ppm of nickel and 800 ppm of vanadium to cracked oil, when carbonized at 693 K, brought about a significant change in optical texture, the coke containing the vanadium (for example) having a mozaic texture ($2\ \mu\text{m}$) compared with a domain texture ($200\ \mu\text{m}$) in cokes from the cracked oil. A similar dehydrogenative polymerization is operating.

Weintraub and Walker [17] co-carbonized anthracene and phenanthrene with biphenyl and noted how progressive additions of biphenyl systematically reduced the graphitizability of resultant cokes. Marsh et al. [18] in a study, using model compounds, of the factors which influence the size of the growth units of anisotropic carbon were able to bring about a reduction in this size by addition of, e.g., thiazole, benzthiazole, phenol, benzoic and naphthoic carboxylic acids, as well as biphenyl. These additions produce the deterioration in optical texture by two processes, one of simple dilution of reactive species and one of early reaction with those molecules capable of forming the liquid crystals (the high molecular weight, low fluidity effect).

This type of experimentation illustrates the delicate balance which exists (during carbonizations to produce anisotropic carbon via the growth of liquid crystals) between the rate of formation of large lamellar molecules capable of forming these liquid crystals, the rate of formation of these liquid crystals from such molecules, and the fluidity and solvent capacity of the carbonization system. Should this balance be disturbed e.g. accelerating disproportionately the chemical reactivity of the molecules in the parent material (by additions of dehydrogenating catalysts such as vanadium, nickel, sodium or potassium metal and chlorides of metals, e.g. FeCl_3) then not only does this enhanced chemical reactivity increase the average molecular weight within the system, it does so at temperatures too low to give this type of system the necessary

fluidity for such molecules to diffuse and re-orientate so as to form the liquid crystals. Consequently, extensive condensation occurs prior to any possibility of significant formation of liquid crystals and an isotropic carbon results. Loss of volatile matter, on further heat-treatment, from such a three-dimensional, random, polymeric structure of lamellar type molecules results in the formation of the microporosity which is responsible for the surface areas as were measured by Mochida et al. [13]. Thus, the chemical process by which addition of potassium salts to coals destroys their caking/coking capabilities must involve an enhancement of the reactivity of the molecules of coal substance such that considerable polymerization is completed at an early stage of the carbonization process. The mechanisms must be similar to those described above.

Additions of fines

In addition to the chemical processes just described which reduce the ability of a system to produce anisotropic carbon, it is also possible so to disturb the system by essentially physical methods. For example, it is established [19,20] that additions of finely divided material such as carbon blacks and catalyst slurry-fines are capable of severely disrupting the process of growth and coalescence of spheres of liquid crystal material. These carbon black particles appear to be "adsorbed" on the surface of these spheres and this prevents any further growth. With sufficient carbon black present the coke can be transformed essentially into an isotropic material. Thus, if sufficient potassium salt, of very fine dispersion (as could be precipitated from an adsorbed solution) is incorporated within the coal substance this effect alone could contribute towards the loss of coking properties.

THE CO-CARBONIZATION OF COALS WITH POTASSIUM SALTS

Mechanistic suggestions

In quite specific terms it appears that nothing of the chemistry which will be involved in these co-carbonizations is to be found in the literature.

There are a few early papers to be found in "Chemistry of Coal Utilization" which appear to be relevant but the objective of these studies was to enhance ammonia production from the distillates. Parker et al. [21] found that CaCO_3 , Na_2CO_3 and FeO increased the yield of ammonia from coal at 920°C but decreased the yield at 815°C . Anderson and Roberts [22] report that NaOH and Na_2CO_3 when co-carbonized with coal eliminated nitrogen from non-coking coals but had no effect on coking coals. Similarly Barber [23] added lime to coal and noted no deleterious effect on the coke. However, these studies were made long before any interest existed in optical texture and should be interpreted with caution.

With no adequate guidelines available from the literature of coal chemistry to elucidate the chemistry of the coal/potassium salt system recourse is necessarily made to putting together a "model mechanism" which can act simply as a starting point for continued discussion.

Perhaps the main reference lead into considerations of the effect of additions of potassium oxide to caking/coking coals appears to be the patents published by Wennerberg [24–27] of Standard Oil Co. (Indiana). (Incidentally, although Mills [1] speaks of additions of potassium oxide to coal, it is rather unlikely that this is the substance as added; either potassium hydroxide or potassium carbonate could be the additive, the potassium oxide formed subsequently by heat treatment.)

Wennerberg reports in his first patent [24] upon the formation of active carbons of exceptionally high surface area by treatment of oxidized cokes with: "e.g. KOH plus a water soluble potassium salt serving as a blocking or defecting agent, until an acid salt is formed. On drying this salt active carbon is produced by the thermal decomposition of the salt which results in the formation of a highly cross-linked carbon structure".

One can only surmise as to the detail of the chemistry of this process but it could be something like the following:

It is probable that several processes are occurring simultaneously in Wennerberg's system. By starting with coke acids additions of KOH will form alkoxides, e.g. -OK and -COOK. Wennerberg then says [27] that: "Thus, treatment of pyrolyzed potassium salt of coke acid in a rotating kiln at 500°C in a stream of equal volumes of steam and argon for 1.5 hours or in a CO₂ stream for 1 hour resulted in the removal of S and H₂S in the exit vapour. After being cooled in a stream of argon and washed with water the active carbon products had B.E.T. values of surface areas of 1759 and 1719 m² g⁻¹". Thus it would appear that the effect of formation of the potassium salts of the acids was to enhance the oxygen content of the system. Some cross-linking would be established which would destroy or reduce the anisotropy of starting cokes. It is envisaged that the oxygen content is extensive (probably >> 5%). During heat treatment in steam or carbon dioxide at 500°C we are probably seeing the thermal decomposition of this chemisorbed oxygen. The lamellar molecules, having been separated and disturbed by the formation process appear not to reform the non-porous anisotropic carbon but to remain somewhat separated to create the micro-porosity which could be responsible for the surface area values of about 1700 m² g⁻¹. The presence of potassium salts (which are leached out by washing) may prevent the complete exfoliation of the oxidized carbon system. It is likely that the treatment with steam or carbon dioxide at 500°C simply introduces thermal dissociation of the chemisorbed oxygen. Significant gasification of the carbon, even in the presence of potassium (a gasification catalyst [28]) at 500°C is not expected.

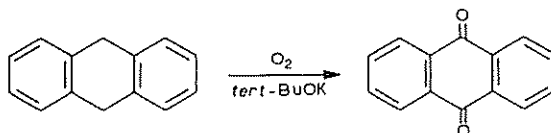
In terms of the coal/K system mentioned by Mills [1] we can have the several processes occurring, incorporating steam and oxygen (residual air may very well be present). The presence of the potassium could perhaps assist in

forming oxygen complexes on the surfaces of the coal by catalyzing the steam—carbon reaction. This oxidation would produce cross-linkage which prevents fusion and caking/coking. Potassium becomes incorporated into functional groups now on the surface and this promotes further condensation processes. Thus, the basic anisotropy of the cokes is not established and the porous, reactive coke (isotropic) results.

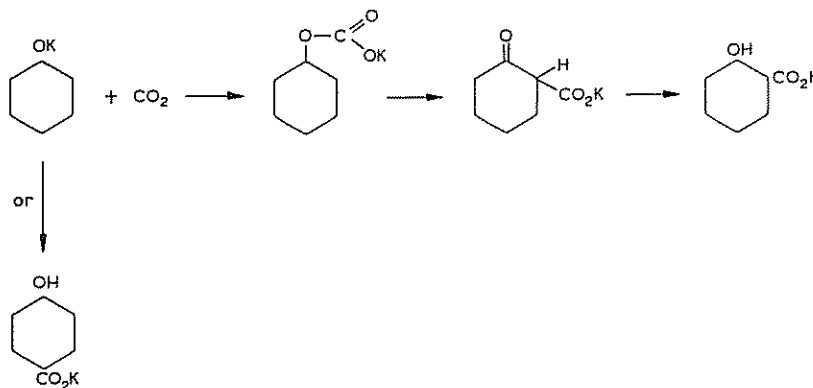
Possible organic reactions

Organic chemists (usually) do not study their reactions under the conditions described by Mills [1]; otherwise they, too, would finish up with a reactive char. Less drastic conditions have to be examined. Guidelines can be found from certain systems.

Rather than use potassium hydroxide, the organic reagent commonly used is potassium *tert.*-butoxide. Its use in syntheses is reviewed by Pearson and Buehler [29]. Very many systems are discussed, but the following is indicative of the processes. It is the formation of an anthraquinone system from a hydroaromatic, and reported more fully by Barton and Jones [30]:



Once the system is oxidized, then the existence of -OH groupings is possible. This leads to -OK groupings. We now have the possibility of a Kolbe synthesis [31] whereby further oxygen can be introduced into the carbon. Very many types of reactions, rearrangements, ring closures are possible involving oxygen functional groups [32] but their immediate recognition in the coal/K/H₂O system is not very practical.



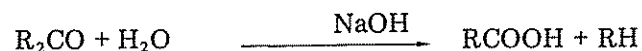
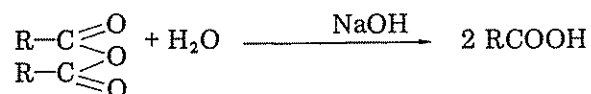
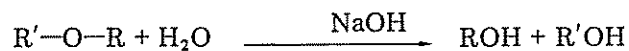
Kolbe synthesis

Kasehagen [33] examined the interaction of aqueous sodium hydroxide on coal (Edenborn, Pittsburgh seam, 84.99% C; 5.86% H; 7.02% O) at temperatures up to 673 K and pressures up to 30 MPa. Concentrations of sodium hydroxide varied from 1 N to 100%. Coke residues were produced at 548 K although the Edenborn coal melts at the higher temperature of 666 K. Use of 5 N sodium hydroxide reduced both the hydrogen and oxygen contents with increasing temperature. Use of 60–80% alkali lowered the oxygen content leaving the hydrogen content unchanged (HTT* 623 K; 60% alkali; 90.16% C; 5.59% H; 2.01% O). Other products consisted of a solid phenolic material of high molecular weight, a viscous liquid of neutral nature, carbon dioxide, free hydrogen and gaseous hydrocarbons. From an analysis of rates of formation and oxygen balances for the carbon dioxide, it was concluded that the reaction in which one oxygen atom of the carbon dioxide comes from the coal and one from the water is the initially predominant one, but falls off rapidly and becomes negligible in the latter half of the run, compared to the reaction in which both oxygen atoms come from the water. Various aliphatic oxygenated compounds behave similarly according to Fry and Butz [34].

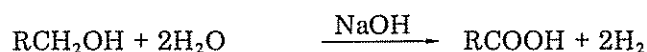
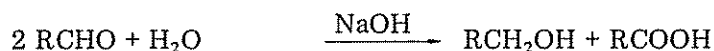
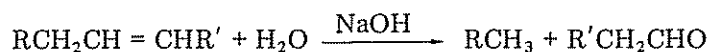
Parker et al. [35] studied the actions of 5 N aqueous sodium hydroxide on a sub-bituminous coal (Elkol, Wyo.; 76.9% C, 5.4% H, 15.9% O) at 523 K over a 24 hour reaction period. Extensive degradation of the coal substance occurred and product analyses can be listed as:

| | |
|--|-------|
| H ₂ , CH ₄ , C ₂ H ₆ | 2.8% |
| liquid phenols | 3.0% |
| solid phenols | 5.0% |
| fatty acids | 13.0% |
| hydrocarbons | 15.6% |
| carbonates (as CO ₂) | 22.0% |
| insoluble residue | 23.8% |

The elemental analyses indicated that the overall reaction corresponds essentially to water addition to the coal. Possible reactions suggested permitting the formation of the phenols, acids, hydrocarbons and the appreciable amount of carbonate which is a feature of this reaction include:



*HTT = Heat Treatment Temperature.



The study of Parker et al. [35] was carried out at temperatures close to the thermal decomposition of the sub-bituminous coal. Brooks and Sternhell [36] used a lower temperature of 463 K for 12 hours and reacted three non-caking low-rank coals (75.2, 70.2 and 68.6% C) with both alcoholic and aqueous alkali. After acidification, the products fused on pyrolysis to give coherent swollen cokes in a crucible test. Ultimate analyses of the products showed a marked increase in the hydrogen content with a small decrease in the oxygen content. It was concluded that the reaction of coal with alkalis was not one of simple hydrolysis.

Sharma and Wilson [37] in a study rather comparable to that of Kasehagen [33] reacted 2 *N* aqueous sodium hydroxide at pressures up to 20 MPa and temperatures in the range 523–623 K with two coals (86.3, 84.3% C). With one coal (86.3% C) the total oxygen content reached a maximum (7.3% from an initial 3.1%) at 523 K to fall to about 2% at 623 K. Some hydrolysis was considered to occur. There was a marked increase in chemical reactivity to oxygen of the solid residue. This could not be attributed to any catalytic action by the sodium because persistent leaching by water to remove the sodium had no effect. The residue had a surface area of 208 m²g⁻¹ compared with 130 m²g⁻¹ in the original coal.

As well as the above chemical changes induced at low temperatures the possibility of disruptive attack by alkali metals derived from sodium or potassium carbonate must also be considered. Hawkins et al. [38] clearly demonstrated the extensive damage to graphitic blast furnace refractory bricks by potassium metal itself. It is suggested that intercalation compound formation and charge-transfer type reactions could be involved.

Ouchi [39] recently reviewed many aspects of chemical studies of coals.

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