Chapter I.
Introduction

The theory of pyrolysis of coal - when coal is heated slowly in a non-oxidising atmosphere, the chemical changes that occur depend on the rank of coal, the temperature, the type of appliance used, the depth of coal layer, etc. etc.

In the neighbourhood of 200°C., the occluded carbon-dioxide, methane and water are completely expelled from the coal, after which an internal condensation occurring in the molecules comprising the essential coal substance gives rise to the evolution of more carbon-dioxide and water. As the temperature is gradually raised olefines, paraffins and unsaturated hydrocarbons predominate at lower temperature while at higher temperature these diminish and higher homologues of benzol are given off. With the temperature further increased, benzol becomes the important homologue and the higher aromatic compounds, e.g. naphthalene and anthracene begin to appear. In the temperature range 200–500°C., the organic sulphur compounds decompose and hydrogen sulphide and certain organic sulphur compounds are evolved. The nitrogenous compounds also break down in this temperature range to yield nitrogen in molecular state, and the hydride of nitrogen as ammonia. The evolution of methane and its higher homologues and olefines also begin at this stage due to decomposition of the essential coal substances. The greater part of the combined oxygen is also eliminated as water and carbon dioxide. Evolution of hydrogen usually begins at 400–500°C.
The yield of gas increases with temperature. At about 300-400°C, the oils begin to appear and the tar is obtained in maximum yield between 500-550°C. The liquids produced from coal at the lower temperature consist mainly of cyclic hydro-aromatic compounds and some higher olefines and paraffin hydrocarbons with very little aromatic compounds of the benzene series, while at higher temperatures, the tar contains quite high proportion of aromatic hydrocarbons.

The quality and nature of gases and tar given off depend not only on the temperature but also on the type of coal, e.g. with lower ranks of coal the yields of tar and gas are high and vice versa. The oxygen content of coals is found to be a very distinctive factor in this connection, since it influences the composition of the gaseous by-products.

Using Gray-King method (1) it has been observed that with high ranks of coal the yield of solid residue is high, while those of tar, moisture and especially of tar are low.

In low rank coals (2), 5-7% of the oxygen in the form of phenolic hydroxyl groups remain attached to the nucleus, while in the case of coking coals this is absent. Upto 5% more of oxygen may remain in other forms, say 1% as quinone groups on the nucleic and the rest in ether links, between nuclei and/or side chains and perhaps in hetero-cyclic rings. To explain its constitution (3), the cluster units of coal, representing a hypothetical molecular model is built around an aromatic nucleus,
Fig. 1
Hypothetical molecular model of coal showing 'cluster' units.
which probably contains on the average about three fused hexagonal rings of carbon atoms in the low rank free-burning coals, slightly more in the good coking coals and perhaps 10-20 in anthracites. This nucleus is surrounded by other nuclei from all sides and one nucleus is joined or bridged to the other directly by C-C linkage, or through ether linkage or by short aliphatic bridges. Average molecule consists of not more than ten such clusters linked together. The shape is flat and extensive with a diameter of the order of 20 Å. Fig. 1.

The changes that take place in coal below 350°C are not easy to follow, though some decomposition is known to take place. It is actually above 350°C that a complete decomposition starts, the actual temperature where it begins depending on the rank of coal. During the initial stage of decomposition small reactive fragments of the coal molecule are broken off. These, then, interact with each other and with the parent molecule in a complex manner. As a result of these complex interactions, the parent coal molecules give rise to slightly smaller molecules which appear in the tar, minute molecules which compose the gas, and highly interlinked large molecules which form the solid residue - coke and char.

J. K. Brown (3) from his studies on the structure of carbonised coal under infra-red has shown that in the temperature range 400-550°C, the coal loses aliphatic and phenolic hydroxyl groups; and the aromatic nuclei which lose these groups
get interlinked with one another to form larger units in the coke. Of course, the possibility remains that a few of the aromatic nuclei are also broken down and volatilised.

In the early stage of the interactions, the products of pyrolysis escape into the capillaries and voids of the coal charge, the secondary reactions involving thermal cracking of the products take place subsequently on the retort wall and modify the products still further.

J. K. Brown and W. P. Wyss (40) determined the hydroxyl content of coals by reaction with acetic anhydride or acetyl chloride. J. D. Brooks and T. P. Meher determined these hydroxyl groups quantitatively by titration with a base in ethylene diamine solution.

All these experiments go to prove that the hydroxyl oxygen amounts to almost a constant percentage of the total oxygen confirmed by infra-red radiation; of course, this percentage has been found to differ according to the method adopted, showing thereby that some of the hydroxyls are either more reactive, or more accessible than the rest.

Phenolic hydroxyl groups in coal not only confer acidic properties to the molecule, but also their presence and that of quinone may influence the chemical bond strength, which in turn exerts an influence on the reactivity of the other parts of the molecule, especially to oxygen, during the course
of pyrolysis, on the colour or on the electrical properties.

The form in which the remaining oxygen exists has not yet been determined with certainty; it may exist either as ether oxygen or hetero-cyclic oxygen and correspondingly the chemical reactivity and the behaviour on heating may be affected.

The relation between the yield of water and phenol to the hydroxyl content of coal offers an interesting subject for discussion. It is extremely likely that during pyrolysis most of these hydroxyl groups will appear either as phenols in the tar, or as water in the aqueous liquor.

From a study of some American coal samples, a comparison has been made by Dryden (5) between oxygen in hydroxyl (calculated as 60% of total oxygen in coal) and oxygen in aqueous and liquor in phenols after carbonisation (700-900°C). It has been assumed that the phenols contain on average 17.5% of the oxygen (as does ordinary phenol) which is a possible average between polyhydric phenols which have higher values and the higher mono-hydric phenols which have lower values.

The agreement between the oxygen in these products and the oxygen in the hydroxyl is worth noting. There is very small proportion of oxygen in the phenol obtained at 500°C, where maximum yield is attained.

So, it may be presumed that the yield of phenols
could be increased very considerably, if the decomposition of
the hydroxyl groups to water could be prevented. In fact, the
yields obtained in the mild hydrogenation process of the Carbide
and Carbon Chemicals Company (6), West Virginia appear to approach
the theoretical.

In this connection, a mention should be made also
of the finding of Wyss (loc.cit.), who found a sharp decrease in
the percentage of "oxygen as hydroxyl" in coals with over 90%
carbon content, though the water yields did not appear to fall
so sharply as the hydroxyl yields.

The course of thermal decomposition of coal is
catalytically influenced by some of its constituents and products
and also by the material of construction of the retort. It has
been observed by R. Lessing (7) that the mineral matters in coal
have a definite bearing on the secondary changes of the primary
decomposition products of coal. This must, no doubt, be ascribed
to catalytic reactions most of which occur in contact with heated
coke. Addition of inorganic compounds to improve the yield of
carbonisation products has been advocated by Lessing, who took
out patents on the process.

The effect of addition of sodium compounds on low
temperature carbonization of coal was examined by Ranich, Lenin
and Korshunov (8). A study of their catalytic action showed that
sodium hydroxide had the greatest effect, sodium carbonate less
and sodium chloride the least in lowering the yield of primary
tar and raising the yield of gas and low volatile liquids. The lighter hydrocarbon fraction in the tar was increased, and the heavier fractions decreased; unsaturated hydrocarbons and hydrogen in the gas increased and methane decreased. The addition to coal of certain salts, e.g., sodium carbonate, sodium borate, ferric chloride, sodium chloride etc., was found to cause variations in the tar produced during carbonisation, increase the reactivity of the coke produced, though the crystallographic properties of the cookes produced were found to undergo little change due to those inorganic reagents.

Patterson (9) found that treatment of coal with 2% of lime and enough steam to cause adhesion increased the yield of gas by about 7%, that of ammonium sulphate by about 2 lb./ton, and that of the liquor by about 11%. The quality of coke was not altered, but the tar yield was decreased by about one gallon, i.e., four and a half litres per ton. These were attributed to the reduction of the amount of retort carbon formed resulting in reduced choking of the ascension pipe.

The formation of bitumens which gives rise to caking properties in coals, by natural hydrogenation of coals with hydrogen sulphide and other hydrogen compounds in the presence of iron sulphide as a catalyst was observed by Sakikawa (10). The catalytic action of pyrites in the hydrogenation of coal was tested and found to be as effective as molybdenum trisulphide or zinc chloride. The effect of pyrites on the coking of coals was also to be beneficial.
Rollason (11) observed that increased production of oil is obtained if coal is carbonised at 500°C. with the addition of 3-5% of finely ground limestone or other carbonates.

M. Letort (12) while investigating the mechanism of combustion of graphite at low temperature (500-600°C) observed that coal ash contains a wide variety of constituents some of which catalyse the oxygen-carbon reaction. Presence of iron in particular appears to decrease the ratio of carbon monoxide to carbon dioxide in the products of combustion.

Jewett (13) claimed production of better coke and illuminating gas by treatment of coal with potassium chlorate and a little potassium permanganate.

In his paper on the banded constituents of coal Lessing (14) observed that durain, vitrain, clarain and fusain behave differently on carbonisation. In general, clarain and vitrain gave higher yields of gas and less of retort carbon and coke than durain. Durain and fusain gave a powdery coke residue, while cokes from clarain and vitrain had a well fused appearance. The mineral matter content of the constituents showed similar differences as regards amount and composition and Lessing held that the differences must, at least in part, be responsible for the differences in the course of carbonisation of the banded constituents.

The influence of added inorganic compounds on the
carbonisation of cellulose, coal and sugar was studied by Lessing and Banks (15). The inorganic compounds were added by both wet and dry methods usually in the proportions of 0.01 gm. mol. per 100 gm. of carbonaceous materials. The effect was an increase in the coke yield, except with iron sulphide, sodium sulphate, nickel carbonate and the oxides of calcium, copper, magnesium and nickel in the case of sugar and oxalic acid alone in the case of cellulose. Remarkable results were generally obtained when salts of strong acids with weak bases were used. The cokes produced differed very much in nature. Compounds which gave a substantially increased coke yield produced swelled cokes by the "wet method" and "compact cokes" by the dry method of addition of the inorganic compounds. But when other compounds were used, the cokes produced were "flaky". The other properties of the coke, e.g. surface structure, true porosity, density, reactivity etc. also were different under different conditions.

Other investigators (16) also found that addition of inorganic compounds considerably influences the course and products of carbonisation.

M. Goswami, H. N. Das Gupta and B. K. Mukherji (17) observed that in the carbonisation of coal, acetylene and other unsaturated simpler hydrocarbons are the primary products from which the aliphatic and aromatic bodies as also the binding substances of coke are finally produced. The inorganic constituents present as catalyst and the catalytic surface of the retort
are the governing factors in influencing the production of these things.

Parker, Kerr and Marson (18) found the addition of Na$_4$CO$_3$ calcium carbonate and ferric oxide to the extent of 2.0% (as oxide) to increase the gas yield by 24% (by volume) and decrease the tar yield by up to 2 gallons/ton.

In their study of the kinetics of thermal decomposition of solid mineral fuels, Smutkina and Kasatochkin (19) observed that the uni-molecular rate and dependence of apparent activation energies on degree of decomposition of a number of high volatile coals, shale and boghead coals under isothermal conditions at various temperature points to the catalytic nature of reactions at relatively low pressure.

Marson and Cobb (20) observed that carbonisation of a coking coal with addition of 5% ferric oxide or sodium carbonate gave a black dense coke instead of a swollen coke. Caustic soda gave a black, powdery coke, while silica, alumina, calcium oxide and calcium carbonate had no effect.

The influence of certain mineral matters on the caking property of coal was also observed by Mielecki (21), who collected data to prove that the caking power of coal was reduced by addition of sulphur, kaolin, calcium carbonate etc. to coal.

Besides exerting their catalytic effect on the pyro-
lysis of coals, the inorganic impurities present in coal have been shown by Fieldner and Selvig (22) to have effect on the fusion point of ash, both under oxidising and reducing conditions. In general, it may be stated that high contents of silica and alumina in the ash raise the fusion point, while high contents of lime and ferric oxide lower the fusion point.

In their investigation on the effect of inorganic additions on the carbonisation of a cleaned sample of Velva lignite in a Fischer retort, Gauger and Salley (23) observed that all additions, except sodium carbonate, which increased the gas yield considerably, decreased the tar yield (especially ferric chloride) and increased the coke yield. Hydrated aluminium and magnesium salts and strontium chloride gave hard chars very different from the soft powdery chars from the untreated lignites, while the anhydrous salts gave soft fine chars.

King and Edgecomb (24) studied the influence of the retort material on carbonisation. They added 5% of many common metals, sulphides and other substances. While coke, carbon, silica, aluminium, chromium and stainless steel had little or no effect, copper, nickel, cast iron and steel became sulphided and reduced the hydrogen sulphide content of the gas as also promoted the formation of hydrogen at the expense of saturated hydrocarbons. Sulphides, e.g. pyrites and marcasites reduced the yield of tar by 11 to 15% and of gas, chiefly owing to non-formation of hydrogen and saturated hydrocarbons. The coke produced was barely coherent.
Marson and Coble (25), Askey (26), Riley (27), Heinze and Farnow (28), Luyken and Bierbraner (29), and Neumann and Ahlen (30) observed that the reactivity of coal or any fuel can be enhanced or altered considerably by the addition of different inorganic reagents.

Gauger and Salley (31) studied the problem in an indirect way. They carbonized in presence of mineral matters sucrose, cellulose or glycine, which unlike coal, can be obtained in a very pure state. They also reported the results of experiments on the pyrolysis of coal from which inorganic matters were only partially removed, and found that by carbonizing coals to which salts or mineral acids were extraneously added the yield of coke generally increased and that of tar decreased. The possibility of catalysed cracking of the volatile materials to carbon has been suggested by Bleyden, Gibson, Riley and Taylor (32) to explain the influence of mineral matters on the trend of carbonisation.

The probability of catalytic mechanism is based on the effect produced by only small proportion of additions - was the observation of Lessing and Bank (33). Bleyden, Gibson, Riley and Taylor (32) concluded that mineral acids may however react stoichiometrically with the organic molecules, causing hydrolysis, scission of groups or cleavage of rings.

Mineral matter in the coal may act as a heterogeneous catalyst; it usually has a composition not far from that of a
cracking catalyst, though the presence of alkali metals or iron might lower its activity. Exposure to high temperatures is also likely to considerably reduce any catalytic activity it might possess, and the effect, if it occurs, is probably of negligible significance.

The coke itself may also have a catalytic action. V. Haensel (34), B. S. Greensfelder, H. H. Voge and G. M. Good (35) showed that charcoal catalyses the cracking of hydrocarbons, and that the distribution of products was identical to that found for gas-phase cracking, whence it is deduced that on this catalyst some radical decomposition chains are important.

D. H. Bangham and N. Berkowitz (36) suggested that the primary product of pyrolysis of coal, before vaporisation first appears as an adsorbed film on the solid phase, where secondary reactions occur, catalysed most probably by the surface of the solid, or material from the gas phase might be re-adsorbed, react on the surface, and then be desorbed.

In the pyrolysis of coal on a commercial scale the oxygen also may act as a catalyst in the form of a bi-radical \(-\text{O-O}\). The presence of oxygen has been found to increase the rate of cracking of petroleum fractions - was the observation of Winward (37). Unlike the mineral matters in coal, oxygen acts like a homogeneous catalyst in the gas phase, starting reaction chains by removing the hydrogen in some such process as follows:—

\[ \frac{1}{4} R - H + O_2 = \frac{1}{4} R + 2H_2O \quad (R = \text{free radical}) \]
The polymerisation of defines and the combustion of hydrocarbons in coal flames are examples of such reaction (38).

Now, the free radical "R" written above joins with another free radical, and then with another and so on, thus forming a chain of radicals in a series of reactions and a trace of oxygen is found responsible for starting this. Many reactions can be made to proceed at a measurable rate at temperatures lower than normal, by the addition of traces of elements that readily produce free radicals or atoms, which start reaction chains.

Hessels, Krejlen and Waterman (39) experimentally verified that when pure methane is passed through a tube at 1170°C with a contact time of 0.07 second or less, no reaction occurs, but if there is some impurity present, e.g. sulphur, or halogen compounds or other aliphatic hydrocarbons considerable reaction occurs giving rise to various unsaturated and aromatic compounds.

In a similar way, during the pyrolysis of coal at all temperatures, the easily decomposable oxygen, nitrogen and sulphur compounds present in the vapour phase are likely to sensitize the reactions of hydrocarbons. Besides this, the presence of traces of oxygen in the industrial retort or oven augments this reaction of sensitization.

Nitric oxide happens to be one of the negative catalysts which inhibit pyrolytic decomposition by removing free radicals (40). But, the proportion of nitric oxide formed within
the retort during the carbonisation of coal on a large scale is not exactly known. It is expected that this compound is formed only in traces due to air leaking into the retort. The course of pyrolytic decomposition of coal is reported to be influenced in a negative way by inorganic catalysts (41).

The classical observation by Lessing (42) of the catalytic influence of some of the coal constituents and that of the retort material on the course of decomposition of coal was corroborated by Bangham (43) also. While Lessing (42) concluded that the composition of the ash, i.e., that of the mineral matters and the contact with the heated coke were the most important factors in bringing about the secondary changes of the primary decomposition product of coal, Bangham (43) propounded that these catalytic changes of the primary decomposition products into secondary ones occur in some definite stages. A number of changes can occur in the solid with either no loss of volatile matter or with loss only of simple molecules like carbon dioxide, water and hydrogen, or by way of decarboxylation, condensation of carboxylic and hydroxyl groups yielding internal esters, dehydrogenation, and rearrangement of carbon frameworks to yield more highly aromatic structures. These changes occur before the volatile matters are released. Prior to the release of the decomposition products as volatile matters, the materials remain trapped inside a particle owing to the smallness of the pores contained in it; and a compact colloidal particle bound
together by primary valence forces could only decompose by a
process of peeling from the surface. Hence the possibility of the
so-called secondary change. Moreover, it is also clear that the
physical structure of coal will have an influence on both the
course and the primary products of its thermal decomposition.
Also, different physical structures and chemical compositions
result in different changes wrought by pyrolysis.

The physical structure of coal and the ambient
fluid have some effect on the products of coal carbonisation. In
general, from more finely ground coal, a greater yield of material
less changed in composition may be expected, because here the
physical barrier which must be overcome by the primary distillates
before they escape from coal is less.

By carbonising a micronised sample of coal at 525°C
in a molecular still, Juettner and Howard (44) obtained a greater
yield of tar, because the escape of volatile matter was easier
by the small particle size. But, the same coal with 20-40 mesh
size yielded less tar. The yield from the coarser sample in the
molecular still was also greater, probably for the same reason
than that obtained from a similar sample carbonised at 525°C.
at atmospheric pressure. This last effect, and the increase in
yield when the rate of heating is increased has been attributed
to solvent action of the liquid products on the coal, since
under such conditions they must remain longer in mutual contact.
It has been found by Schenk (45) that more tar is obtained when
coal is carbonised in the presence of added mineral oil or tar. This mechanism may be regarded as a mild chemical reaction between the coal and the liquid.

Importance of Low Temperature Carbonisation and its products: The temperature usually employed in low temperature carbonisation ranges between 425-600°C. The high yield of liquid by-products and the low cost of production of semi-coke have stimulated interest in low temperature carbonisation of coal since a long time. The decomposition of volatile matter is minimum at this temperature and the yield of gas is relatively low, but of much higher calorific value than the high temperature gas, with a maximum yield of tar and oil distillates.

The properties of the tar yielded by coals carbonised at different temperatures vary. In low temperature tar, the same kind of hydrocarbons are present (even including benzene about 0.5% of tar), though in very small quantities, as are found in the tar obtained from high temperature carbonisation. But, the hydrocarbons of low temperature tar are of higher molecular weight and contain in addition saturated, unsaturated and poly-methylene hydrocarbons. The saturated hydrocarbons rarely exceed 6% consisting chiefly of solid paraffins.

The high content of tar acids (up to 35%) is another characteristic of low temperature tar. These tar acids are
generally of higher molecular weight than the tar acids obtained from gas retorts, or coke ovens; the lowest member is phenol. It is at 550°C, that the largest production of tar acids is obtained. This high yield of tar acids is balanced by the lower calorific value of the low temperature tar. The quality of tar also depends to some extent on the type of oven or retort used.

The most notable characteristic of low temperature semi-coke is that it is non-friable and free burning. It is readily ignitable, burning with a non-luminous flame without producing any smoke, as its volatile matter content (9-11%) is rich in hydrogen. This is why, it is suitable for domestic purposes.

In the present series of experiments, some attempts have been made to study the effects of mineral matters present in coal on the products of low temperature carbonisation. For this purpose, samples of coal have been washed in flotation cells to remove the mineral constituents as far as possible, prior to carbonisation. The nature of the minerals have been studied and the tar and gas obtained have been analysed.

In Indian coals, apart from the main constituents of ashes, e.g. alumina, silica, titanium dioxide, magnesium oxide, ferric oxide, calcium oxide, B. Mukherji and R. Dutta detected the presence of silver, boron, beryllium, cobalt, copper, gallium, germanium, lithium, molybdenum, nickel, lead, scandium, vanadium, tungsten and zirconium by means of spectrum analysis.
Since long it is known that when any mineral matters are present in coal or when some more are added to it, they play their influence on the products of pyrolysis of coal. They not only act as diluents, but exert definite catalytic effect on carbonisation, combustion, chemical reactions etc. etc., though not affecting the crystallographic properties of the coke.

The surface or wall of the retort also act catalytically during the pyrolysis of coal, especially in the formation of different hydrocarbons, ammonia and amino-bodies.

So, if samples of Indian coals containing various amounts of mineral matters are prepared by washing, the different amounts and nature of the mineral matters present in these prepared samples will be expected to exert varying degrees of catalytic effects on the products of carbonisation. The floats may be assumed to be that fraction of coal from which mineral impurities have been partially removed, and the sinks to be those fractions in which the proportion of mineral matters has been concentrated. The high yield of liquid products normally obtained during the low temperature carbonisation of coal provides a suitable source of raw materials from which various refined chemicals can be manufactured, and the yield of some of them can, perhaps, be still increased by adopting suitable catalytic methods after cleaning the coal to various degrees by washing.

Flotation of coal to remove mineral matters: The problem of removal of mineral matters and impurities present in coals has ever since engaged the attention...
of many workers in India and abroad. In recent times investigations on washability of Indian coals are being carried out at the Fuel Research Institute, Jealgora. As early as in 1924 a number of samples of Indian coals was tested in a laboratory type froth flotation plant and the results thereof were published by Randall (46). But, these results, on the whole, were anything but encouraging. Randall tested 24 samples of finely pulverised coals from different seams of the same bed. The ash contents of the samples varied between 12.7% and 23.4%. It appears from a summary of his work by Forrester (47) that yields varying between 48% and 82% of clean coal with 15% ash content could be obtained.

The necessity of size reduction to about -20 mesh before washing was first suggested by Randall. This was partly supported in a subsequent report of the Fuel Research Committee (48). The Gondwana coals undoubtedly presented special difficulties. Randall's disappointing results, although obtained within a narrow range of selection, probably created a pessimistic outlook regarding the amenability of Indian coals to cleaning.

In 1932, Bose and Gupta (49) carried out float and sink tests on certain Raniganj and Jharia coals containing 15% ash. They concluded that a 5% reduction in ash could be obtained by rejecting about 25% of the input.

Forrester (47) made some laboratory scale experiments with samples of Jharia coal crushed to pass a 0.25 inch screen.
The ash contents of the original coals varied between 8.66% and 23.5%. With the exception of three coals having 8.66%, 10.1% and 10.69% ash, respectively, it was found that from a coal of 22.14% ash content, yields ranging from 18% to 92% of clean coal having 10% ash could be obtained.

Later, Forrestér and Majumdar studied Indian coals by float and sink methods and opined that a better quality of low ash coal gives in general a high output of low-ash clean product. It appears from their data that at a particular ash content the output does not necessarily bear a direct relation to the ash content in the raw coal. There are however exceptions. If the ash in the original coal is appreciably above 24%, then the yield of clean coal containing 16% ash falls off rapidly.

R. E. Zimmerman (50) described experiments to determine the extent to which fine coals are amenable to flotation. Some aspects of the cleaning of fine coals by flotation have also been studied by G. T. Bator (51).

J. R. Prentice (52), D. R. Mitchell (53), E. T. Wilkins (54), J. Stafford (55) and others also studied the possibility of cleaning of fine coals by froth flotation. The wetting agents used to obtain high percentage yield of coal concentrates have also been the subject of many patents (56). B. I. O. S. report (57) describes a method for obtaining very low ash coals by primary and secondary jig washing followed by froth flotation in the final stage, combined with caustic soda.
pressure extraction. From coals of size 12.5 m.m. and 22\% and 12\% ash electrode carbons were thus produced. The resultant yield was roughly 24\% coal with 0.28\% ash.

A British Patent (58) describes the froth flotation of coals 1/16th inch size, with high ash content, using water soluble sulphonate or bi-sulphate of an alkali metal or ammonium salt.

Kitson and Company used a method (59) in which an oil in water emulsion with or without emulsifying agents was used for producing a coal froth. This was added either to a slurry of coal or to the water used. G. T. Bator (51) treated a sludge of particle size less than 10 mesh, with kerosene to flocculate the coal.

H. Menzel (60) studied the effect of particle size on flotation and the efficiency of medium and light coal-tar fractions and of benzol as flotation agents. It was found that less flotation agents were needed when everything above 0.75 m.m. was screened out. The specific effect of varying particle sizes on flotation of bituminous coal slurry is, however, not fully understood.

G. B. S. Luthra, S. Ranga Raja Rao and A. Lahiri (61) working at Fuel Research Institute, Jealgora, India published some data on the effect of particle size of coal on their flotation characteristics using cresylic acid, creosote oil, oleic acid, cod-liver oil, shark liver oil and pine oil as flotation agents.
They found the flotation to improve by fine crushing, the optimum size range lying probably between 72 and 120 mesh. Regarding the reagents, varying results were obtained and it was recommended that the best reagent for any specific coal had to be found by trial.

E. T. Wilkins (62) described a two-stage process for production of ultra-clean coal (1.5% ash) from coal containing 12% ash. He adopted heavy media magnesite suspension followed by froth flotation after re-crushing to 0.2 m.m. and used far oil fraction (b.pt. 270-300°C.) as flotation agent.

H. G. Graham and D. Schmidt (63) also described methods of producing ultra-clean coal for electrode carbon.

Hancock (64) discussed the uses of washability curves and of Fraser and Yancy formulae for determining the efficiency of coal cleaning operations. It has been shown that the operation mainly depends on density differences and the above formulae are not strictly applicable where size differences also operate.

In Elmore vacuum flotation process (65), prevalent in Europe, fuel oil is used as reagent for coal slurry in a vacuum cell. The vacuum draws out the dissolved air from water and slurry and thereby a froth is produced. The power required for vacuum has been found to be less than that required for agitation. The froth is also found to be stable and can therefore be easily dewatered.
Ralston and Wichman (66) established a relationship between the flotability and the ranks of coal. Brody and Ganger (67) dealt with the angle of contact of gas bubble for anthracites (48°), bituminous coals (60°) and lightite (90°).

Patrick, F. Whelan and David Simpson (68) showed that improved recovery and concentration grade can be obtained by addition of such reagents as dilute dispersions, e.g. one part of reagent to 50 or more parts of water. This, in their opinion helps to avoid localised concentration, which cause variations in recovery and concentrate grade.

Denver (69) has described a technique for preparation of coking coal from high ash (20%) coal and also for separation of low-ash fines contaminated with high ash materials as a result of mechanical mining. The sequence of operation in this technique is jigging, dewatering, conditioning with kerosene and pine oil and flotation. The economics of upgrading, coal washery slurry by froth flotation has been discussed by J. Stafford.

P. Moiset (70) studied flotation of -14 mesh coal fines in a 500 gm. laboratory type Denver Sub-aeration cell. The feeds consisted of a 20% slurry with 20-60% ash. The reagent was principally cresylic acid, but kerosene and pine oil were used in some of the tests. With 20% ash in the feed (-14+20 mesh) particles could be floated to give 4.52 - 5.36% ash in the product with 90-95% recovery of coal substance. The ash rejection and coal recovery could be increased by lowering the particle...
size, but the ash content in the float was found to increase simultaneously or correspondingly. The reagent consumption had little effect on the low ash feeds. With high-ash feed, the use of increasing amount of reagent increased both the ash content of the product and the recovery of coal substance in practically all the ranges of particle size. In unsized feeds the various particle size fractions behaved independently.

Adoption of flotation principle is, therefore, considered a plausible means for recovery, at low cost, of low-ash coal from 1/8" down to 200 mesh size. Kerosene, and other petroleum products with pine oil or alcohol frother, are the reagents generally recommended.

Cresylic acid frothers, coal tars, cresols and wash waters from scrubbling towers have also been used not only as selective frothers, but also for safe disposal of obnoxious constituents which often get absorbed in coal. Lime additions have been made with flotation feed to enable removal of fine pyrites, present free in coal.

Trent (71) obtained a patent for recovery of clean coal. The physical phenomena involved in the process has been explained by Tegart (72). In this process the finely ground coal is agitated with water and oil, and the oil-coal aggregates or granules thus formed are separated from water, which retains the mineral particles. The use of fuel oil, crude oil, benzol or gasoline upto one half the weight of the carbonaceous content
of the raw coal is recommended in this process. The Trent process is related to some earlier parent inventions for which patents were issued to Cattermole (73) as early as 1904. A specification for the viscosity of the oil to be used was worked out by Ralston (74) as follows: The more viscous the oil, the higher the recovery and the lower the ash rejection. This has been found to be applicable when dealing with coal particles of -300 mesh size. The effect of chemical composition of the oil is not definitely known but it has been recorded that the operation of the Trent process is improved when a small amount of oleic acid is present (75).

The beneficiation of non-metallic ores depends mostly on the use of various flotation reagents at different pulp conditions. A general characteristic in non-metallic minerals is the occurrence of basic minerals in association with acidic minerals, and so a separation is considered effective when a single basic-type mineral is floated from one or more acidic type mineral. The success of such flotation separation much depends on the feasibility of grinding the ore to the desired size. Problems often arise when the association of minerals is very intimate or the texture of one or both is such that the minerals cannot be entirely opened up or liberated, i.e., when the matrix cannot be separated from the recoverable constituents, by grinding.

"The success of an experiment on flotation of coal depends largely on experience" - was postulated by Madell (76).
And according to Luyken and Biarbraner (77) the principal independent variables in flotation practice are (i) reagents, (ii) time, (iii) temperature, (iv) pH and (v) particle size. Besides the reagent itself, a small increase or decrease in its amount and its mode of addition have been found to frequently modify the results of flotation. Grinding condition and extent of aeration also influence the result. Hence the practical difficulty encountered in a detailed study on froth flotation is the fact that it is not always possible to alter any of the variables without affecting another.

Eveson, Ward and Worthington (78) observed that though it is not possible to forecast with certainty the specific behaviour of a coal in a commercial cell from the results obtained in a laboratory cell, yet some general conclusions can be drawn.

Eveson, Ward and Worthington (78) maintained that the process of flotation they adopted was not very sensitive to changes in the pH value of the pulp over the range pH 5 to 9, and control of the pH value would not give a justifiable improvement in separation. A slightly better separation at pH 9 than at pH 5 was observed by them. This result corresponds to that of Davies (79) who found that pH 8 - 8.5 provided the best conditions for froth flotation of coals. Allum and Whelan (80) also reached a similar conclusion.

Stewart (81) used lime or sulphuric acid to the
flotation circuit of coal in amounts large enough to vary the pH from 2 to 11.2; the greatest reduction in sulphur content occurred at pH 10.3, but this was accompanied by a reduced yield of coal. Optimum condition from the point of view of both yield of coal and reduction in sulphur and ash content were reached with a neutral circuit.

Eveson, Ward and Worthington (loc. cit) also observed that a change in the duration of conditioning time from two to four minutes had little effect on the results of froth flotation. Although slightly better separation was obtained by them when a conditioning time for pH adjustment of two minutes was used instead of 4 minutes, the optimum conditioning time might well be between zero and two minutes. A shorter conditioning time helps to reduce the extent of clay dispersion and the possibility of slimes coating the coal particles; it would also reduce the amount of reagents absorbed by the coal.

Allum and Whelan (80) working with a low rank Warwickshire coal observed that conditioning time should not be unduly prolonged. Optimum time was probably less than two minutes. They were of the opinion that the pH during the conditioning time was the deciding factor in the success of flotation separation.