

Mathematical Modelling of Volatile Matter Evolution During Carbonisation in Metallurgical Coke Ovens

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ABSTRACT

The carbonisation mechanism in the coke oven chamber is quite complex and, although much useful information has been generated by empirical studies on both industrial batteries and pilot ovens, attempts to mathematically model the coke oven phenomena met with only limited success. In this study, a mathematical model to simulate volatile matter evolution during the carbonisation process for Indian coals has been developed. This model is a part of the endeavour to develop a rigorous mathematical model to simulate the main physical, chemical changes and transient heat transfer phenomena occurring during thermal decomposition of coals in coke oven carbonisation. To have sufficient generality for the applications to coke oven practices, the mathematical model describes the kinetics of release of main volatile matter constituents, thereby permitting the changes in the mass and composition of solid residue to be estimated by element balances. The prediction of volatile matter evolution has been made from coal ultimate analysis and heating profile based on the principles of kinetics and rate phenomena. The aim of this mathematical model is to predict the yield and composition of volatile matter as a function of charge temperature and to relate these to the changes in the semi-coke composition for some typical Indian coals used for coke making in the coke ovens of Tata Steel. The quantity of volatile matter loss from coal

during carbonisation was also determined experimentally using a standard thermogravimetric analyser (TGA), in which the weight of the sample undergoing test is monitored continuously while the sample is heated at a constant rate. The computer based mathematical model predictions for volatile matter yield are verified with the experimental results and found to be in good agreement.

Key words: thermal processing, metallurgical coke making, process modelling, rate phenomena, volatile evolution

1. INTRODUCTION

Commercial production of coke is a part of virtually every integrated steel making operation. Stabilisation in metallurgical coke quality and reduction in carbonisation heat consumption are of prime importance to coke production technology. The production of pig iron in the blast furnace utilises coke as both the fuel to generate the high temperatures required to produce separate liquid pig iron and slag phases and the carbon source for reducing the solid oxides. In view of the techno-economics of pig iron production, steel plants throughout the world have installed blast furnaces of large capacities. These furnaces have placed heavy demands on the quality of coke and in particular the

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Coke Strength after Reaction (CSR), Coke Reactivity Index (CRI) and Micum Indices in order to ensure low reactivity and high strength at elevated temperatures. Although most of the coke ovens in the world follow the top-charging route, some plants in India have adopted the stamp charging technology for production of coke for blast furnace operation. The compulsion to adopt the latter route arose from the lack of reserves of good quality coking coal in India; the coke produced by the top-charging route thus may be detrimental to blast furnace operation and stability in view of its poor CSR and Micum indices. The stamp charging method results in gainful utilisation of poor coking coals suitably blended with imported coals with better coking characteristics.

The basic philosophy of coke making is to produce high quality coke and provide safety for the ovens. The need for changes in coking practice in the coke oven of integrated steel plants involves new blend formulations, different carbonising conditions, or even departures from conventional oven design. Although the effects of such changes can be assessed using experimental coke ovens, such tests are expensive and time consuming. An alternative is to describe the changes in a coke oven by means of mathematical models /1-4/, supplemented with the experimental results of the pilot oven as and when required.

The primary objective of this study (which is part of a rigorous mathematical model to simulate the processes of thermal decomposition of coal during carbonisation) is the development of a computational procedure to predict the phenomena of volatile release and composition of the volatile matter and to relate these to the changes in the semi-coke composition from first the principle, and ultimately analysis of coal and heating profile as inputs.

2. THE CARBONISATION PROCESS

The carbonisation process during coke making has remained basically invariant for a long time. Coals crushed so that about 80% of the particles are less than 3 mm in diameter, are either charged from the top or stamp charged, using a stamp-charging and pushing (SCP) machine, into slot-type ovens. A battery can

contain several ovens. The ovens are heated indirectly through the side-walls, which are usually made of silica refractory brick. Between the walls of adjacent ovens are flues through which the combustion products of the fuel gas pass, maintaining the oven wall at a temperature in the range 1373 K to 1573 K. Fig. 1 and Fig. 2 show the stamp-charged coke oven with SCP machine and top charged coke oven batteries of Tata Steel, Jamshedpur, India.

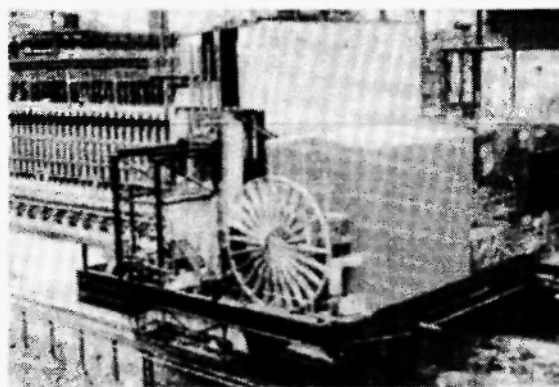


Fig. 1: Stamp-charged coke ovens

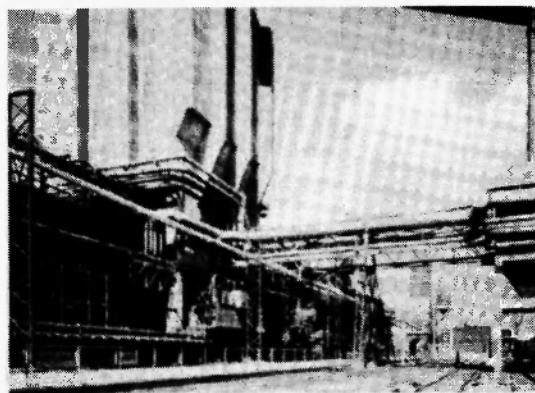


Fig. 2: Top-charged coke ovens

The coal near the oven walls is heated rapidly and heat is then gradually transmitted through the charge. When the charge attains 373 K, the moisture is considered to be converted to steam. As the temperature increases rapidly and the charge attains a temperature between 623 K and 673 K, a good coking coal will

soften and then begin to decompose. As heating continues, the particles coalesce to form a coherent porous structure. The duration of this plastic stage is comparatively short, generally lasting little more than 373 K, after which re-solidification takes place. The resulting semi-coke contracts, setting up differential strains and causing fissures to form perpendicular to the side walls. As these contractions occur, volatile matter continues to be evolved and the semi-coke is gradually transferred into a brittle coke. When the charge centre temperature has reached 1173 K, a further period of up to three hours is allowed as a heat soak; the total carbonising time can vary between 18h to 24 hours. The release of volatile matter has a substantial effect on the heat transfer and thermo-physical properties of the charge during carbonisation /16,17/.

3. MATHEMATICAL MODEL FOR VOLATILE MATTER EVOLUTION

Pure coal (i.e. excluding moisture and mineral matter) is an organic substance mainly consisting of carbon, hydrogen and oxygen, with smaller amounts of nitrogen and sulphur also present. The molecular structure of coal has been the subject of intensive study by a variety of techniques. The evidence indicates that coal is basically aromatic in structure. Cluster units containing typically three to five condensed rings are linked to each other in groups of up to ten, and stacked parallel to each other to form crystallites. Short aliphatic side chains and bridges are attached to the aromatic cluster units, and alicyclic structures are also present. The release of volatile matter is an important stage in coal conversion processes /1,2/. In some cases, the evolution rate and composition of volatile matter are themselves of direct interest, but of more general significance is the impact on the physical properties of the coke or char residue. During thermal decomposition of coal, temperature is increased to 1273 K. The coal mass decomposes physically and chemically while liquid and gaseous products volatilise. In order to understand this process, the reaction kinetics of coal particles has to be investigated properly. If the coal particles are larger, heat and mass transfer as well as secondary reactions have additionally to be taken into

account. Probably the most fundamental mathematical description of the kinetics of volatile matter evolution is that of Chermin and Van Krevelen /5/. The following scheme of reactions, assumed to be first order, to describe the thermal decomposition of a coking coal was proposed:

Coal \rightarrow Metaplast

Metaplast \rightarrow Semi-coke + Primary volatiles

Semi-coke \rightarrow Coke + Secondary volatiles

where, the term 'metaplast' refers to an unstable fluid form of coal. It was also found that temperature dependence of rate constants could be correlated by the Arrhenius equation. It was reported that activation energies of about 200MJ/Kmol were used for the first two equations but, for secondary volatile matter evolution stage, the activation energies increased from 200 MJ/Kmol to 450 MJ/Kmol. One of the disadvantages of this approach is that the unstable intermediate residue species necessary for the reaction scheme, i.e. the 'metaplast' and 'semi-coke', do not have readily identifiable physical properties or chemical composition. This approach has the disadvantage that the unstable intermediate 'metaplast' and 'semi-coke' may not have readily identifiable chemical composition and physical properties.

The chemical decomposition process of a coal during thermal processing is commonly modelled by multiple reactions /14,18-20/, which act independently of each other. Campbell and Van Heek /8,9/ developed a model to simulate the rate of formation of a single gaseous product on the basis of independent reactions. The mathematical formulation was based on a generalised differential equation of the following form:

$$\dot{y}_{ij}(t) = \frac{dy_{ij}(t)}{dt} = k_{ij}(t)[y_{ij\infty} - y_{ij}(t)]^n \quad (1)$$

Here $y_{ij}(t)$ denotes the yield of gas i in reaction j per gram coal at time t with total yield $y_{ij\infty}$ at the end of the reaction. The exponent n indicates the order of the reaction, which is usually equal to one. The number j of ordinary differential equations depends on the number of maxima of the reaction rates, which are observed usually one to three. At the beginning of the reaction, there is no gas: $y(t_0) = 0$. The kinetic parameter $k_{ij}(t)$ of reaction j of gas i is of Arrhenius form

$$k_{ij}(t) = k_{oij} \exp\left[\frac{-E_{ij}}{RT(t)}\right] \quad (2)$$

With frequency factor k_{oij} and activation energy E_{ij} R denotes the gas constant and $T(t)$ the temperature. The unknown frequency factors k_{oij} , the activation energies E_{ij} as well as the total yields $y_{ij\infty}$ were estimated using observations taken during the pyrolysis process and literature information. This approach was extended by Pitt /12/, where he considered coal as a mixture of many components, which decompose independently, and it was assumed that the decomposition reactions are again of first order. But instead of increasing the number j of parallel reactions, a wide range of activation energies was supposed. The number of molecules with activation energies between E and $E+dE$ is proposed to be proportional to $f(E)dE$ where $f(E)$ denotes the well known Gaussian distribution. Integration of equation (1) yields,

$$y_{ij\infty} - y_{ij}(t) = y_{ij\infty} \exp\left[-k_{oij} \int_{ta}^t \exp\left(-\frac{E_{ij}}{RT(\tau)}\right) d\tau\right] \quad (3)$$

for one particular reaction and,

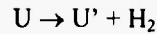
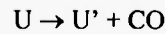
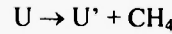
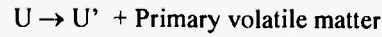
$$y_{i\infty} - y_i(t) = y_{i\infty} \int_{t0}^{\infty} \exp\left[-k_{oi} \int_{ta}^t \exp\left(-\frac{E}{RT(\tau)}\right) d\tau\right] f_e(E) dE \quad (4)$$

for the total amount. In addition to the effective volatile content y_{i1} of gas i , the mean activation energy E_0 , the standard deviation σ_E and, as in some cases, the mean frequency factor k_{00} and the standard deviation $\sigma_{\log k_0}$ of the Gaussian distribution functions are constants of this model.

3.1 Mathematical Model Formulation

The present formulation is based on certain assumptions with a generalised formulation as described earlier /8,10/. It is assumed that the evolution of volatile matter can be described by four parallel reactions defining the release of the primary volatile matter,

methane, carbon mono-oxide and hydrogen



where, U and U' denote the solid phase (coal, semi-coke or coke) before and after the reaction, respectively. The primary volatile matter is defined as Tar, H_2O , C_nH_m , CO_2 , N_{vol} and S_{vol} species.

Provided that the composition and rate of evolution of each of the volatile matter species can be predicted, the mass and composition of the charge can be calculated from that of the coal by mass balance. This methodology forms the basis of the present model. For keeping the analysis mathematically tractable, it is desirable that only the compositions of the coal blend in terms of carbon, hydrogen, oxygen, nitrogen and sulphur would be considered. Other elements are known to occur in coal, but amount to less than 0.3% and are, therefore, ignored. The composition on the basis of ultimate analysis for typical coals used in Indian steel works has been used in this study. A generic formulation has been attempted. The kinetics of volatile matter release can be described by a system of parallel first-order reactions /1,13,14/, for which the rate constant varies with the temperature according to Arrhenius relationship in a generalised framework.

$$\frac{d\delta}{dt} = [\kappa \exp(-E/RT)] (1 - \delta) \quad (5)$$

where, δ is the fraction of the component of volatile matter released by time t , κ is the frequency factor, E is the activation energy, R is the gas constant, and T is the temperature in Kelvin (K). Each of the volatile matter species can be subdivided into components corresponding to different activation energies and the release of each of these components is assumed to be described by equation (1). Although the activation energies for the volatile matter species correspond approximately to Gaussian distribution, however, a transformed Rossin-Rammler function has been used instead, to describe the distribution more accurately /1,6,7/:

$$F_j(E) = \text{Exp}\left\{-\left(\frac{E - E_0}{\alpha}\right)^{\beta}\right\}; \quad (j = 1, N) \quad (6)$$

E_0 , the 'starting activation energy', α and β vary both with species and coal rank which is available in literature [1,16,17]. N is the number of species to be considered in the volatile matter. For the j^{th} volatile matter species, the cumulative amount m_j expressed as a fraction of dry ash free (*daf*) coal released at a time t is given by

$$m_j(t) = \overline{m_j} \int_0^1 \delta(t, E) dF_j(E) dE = -\overline{m_j}; (j=1,2,\dots,N) \quad (7)$$

where, $\overline{m_j}$ are the final yields (as mass fraction of *daf* coal) of coke for the j number of species. Therefore, the rate of release of species is given by the differential equations,

$$\frac{dm_j}{dt} = \overline{m_j} \int_0^1 \frac{\partial \delta}{\partial t} \frac{dF_j(E)}{dE} dE \cdot (j = 1,2,\dots,N) \quad (8)$$

Using eqn (5), the rate of release of species can be described as:

$$\frac{dm_j}{dt} = \overline{m_j} \int_0^1 \kappa \exp(-E/RT) (1-\delta) \frac{dF_j(E)}{dE} dE; \quad (j = 1,2,\dots,N) \quad (9)$$

Equations (7), (8) and (9) can be solved with a given heating profile (heating rate) by numerical method to predict the kinetics of release of the number of volatile matter species considered in the model as a function of charge temperature.

The cumulative masses of the volatile matter species, $m_j(t)$, $j=1\dots N$, at time t calculated from equation (7) can be used to determine the mass of char remaining at time t , $m_0(t)$ by an overall mass balance

$$m_0(t) = 1 - \sum_{j=1}^N m_j(t) \quad (10)$$

The composition of the char residues at time t can be calculated by element balances denoting the mass fractions of carbon, hydrogen, oxygen, nitrogen and sulphur in the char at any time t by $y_i(t)$, $i = 1\dots 5$, which can be presented as [1,17,20] systems of simultaneous algebraic equations;

$$y_i m_0 + \sum_{j=1}^N A_{i,j} m_j = b_i \quad i=1,\dots,5 \quad (11)$$

which can be written as,

$$y_i = (b_i - \sum_{j=1}^N A_{i,j} m_j) / m_0 \quad i=1,\dots,5 \quad (12)$$

The values of $A_{i,j}$, $i=1,\dots,5$ and $j=1,\dots,N$ represent the analysis of coke and volatile matter species, expressed as mass fraction of carbon, hydrogen, oxygen, nitrogen and sulphur. The values of b_i $i=1\dots 5$ represent the ultimate analysis of *daf* coal.

As stated earlier, the present analysis assumes primary volatile matter to be constituted of tar, CH_4 , C_2H_6 , H_2O , CO_2 , NH_3 and H_2S , and CH_4 , C_2H_6 can be represented in the generic form as C_mH_n . Therefore, N has been taken as 6 ($N=6$) as the number of species considered in all pertinent equations having the species index N . Previous experimental studies have [6,7] established that the evolution of the first five of these species occur below 823 K. Although investigations have shown that some hydrocarbons and CO_2 are still present above 873 K, the quantities are small and these species are not included as primary volatile matter. Because the release of volatile matter occurs rapidly, changes in composition only have a transient effect on the prediction of semi-coke composition. It is, therefore, assumed in the model that the primary volatile matter can be treated as a mixture of constant composition, the release of which can be described by single reaction given above. As noted in previous studies [21,22], proportions of secondary volatile matter species produced above 873 K cannot be assumed constant. Methane predominates at the lower temperature, whereas hydrogen becomes important in the final stages of carbonisation. The evolution of these species is therefore described by separate reactions for CH_4 , CO and H_2 .

3.2 Volatile matter evolution measurements:

The rate of volatile matter loss from coal during carbonisation was determined experimentally using both pot and tubular furnace and standard Thermo Gravimetric Analyser (TGA), in which the weight of the sample undergoing test is monitored continuously while the sample is heated at a constant rate. Experiments were carried out on a 75mm steel pot up to 1223 K for

Jamadoba (Coal A) and West Bokaro (coal B) coals with particle sizes as used in the Tata Steel coke ovens. Soaking time for all the experiments were kept at 1 hour. Weights of the samples prior and after the experiments were measured to determine the yields. A schematic diagram of pot furnace experimental apparatus is given in Fig. 3. Final weight losses were measured to estimate the cumulative yield of volatiles with necessary correction for ash in the coal. The application of these techniques to coal research is well established [6,11,15,16] and need not be elaborated here. The TGA tests were carried out on Indian coals A and B. The characteristics of two type of Indian coals used in the coke making at Tata Steel has been considered for both simulation and experiments. The details of analysis for these coals are given in Table 1. The heating rate of charge for both simulation and experimental tests is taken as 3 K/min. The model predictions and experimental results are presented in Tables 2 and 3. The experimental cumulative release rates of different species of volatile matter contents cited from literature [1,7,14,15] for two British coals are depicted in Table 4 for comparison of predictions.

Table 1
Analysis of coals

Proximate Analysis (mass %)			
	Ash	VM	FC
Indian coal-A (West Bokaro)	16.95	25.80	57.25
Indian coal-B (Jamadoba)	17.09	21.81	61.10

Ultimate Analysis (dry ash free basis) mass %					
	C	H	O	N	S
Indian coal-A (West Bokaro)	84.63	5.31	1.87	0.74	7.45
Indian coal-B (Jamadoba)	85.20	5.13	2.32	0.81	6.74

3.3 Numerical implementation

For the implementation of the mathematical models, an interactive FORTRAN code, named as Coke Oven Simulation-1 (COKESIM -1) has been developed to solve the governing equations (7-12) of the model, by

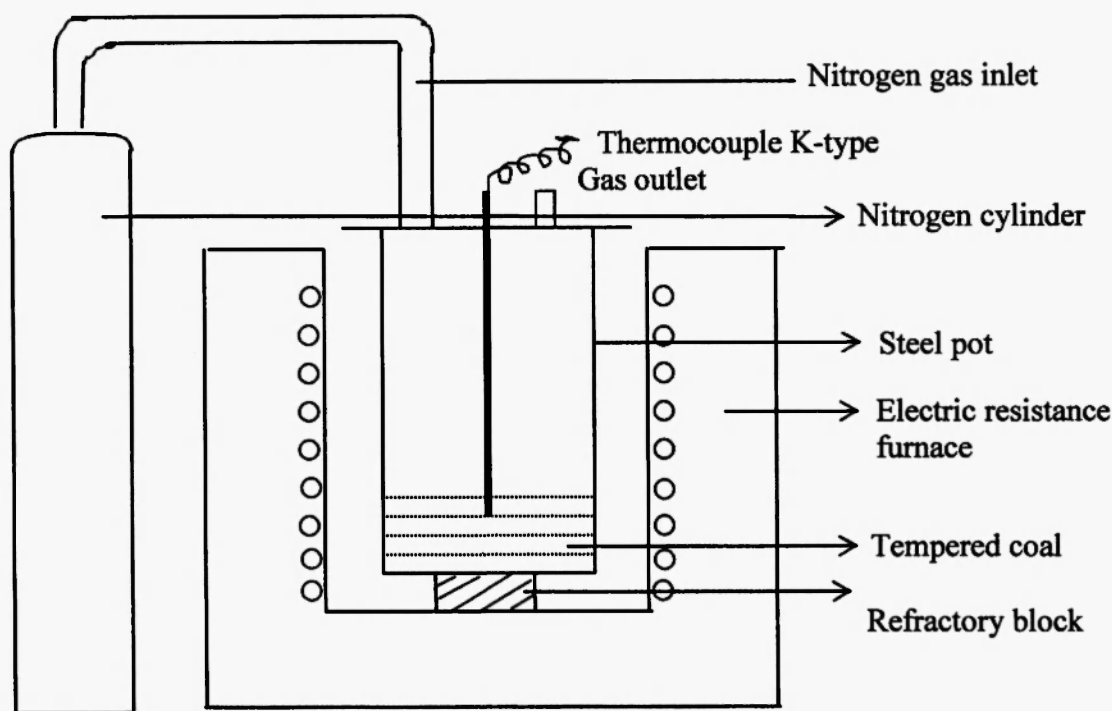


Fig. 3: Schematic of pot furnace experimental apparatus

Table 2
Experimental validation of computer predictions for coal A
(Mass fraction basis)

Charge temperature (K)	Computer Simulation	NML TGA experiment corrected for dafb	CCT lab (Tata Steel) experiment corrected for dafb	NML pot furnace experiment corrected for dafb
773	0.190	0.205	0.20	
973	0.270	0.291	0.242	
1173	0.304	0.329	0.320	0.309(final)

Table 3
Experimental validation of computer predictions for coal B
(Mass fraction basis)

Charge temperature (K)	Computer Simulation	NML TGA experiment corrected for dafb	CCT lab (Tata Steel) experiment corrected for dafb	NML pot furnace experiment corrected for dafb
773	0.165	0.183	0.170	
973	0.232	0.261	0.213	
1173	0.278	0.290	0.274	0.276

Table 4
Cumulative release rates of volatile matter cited from literature for British coals (Mass fraction basis)

Temperature (K)	Methane		Carbon monoxide		Hydrogen	
	Coal X	COAL Y	Coal X	Coal Y	Coal X	Coal Y
723	0.002	0.003	0.001	0.001	0	0
823	0.021	0.021	0.002	0.004	0.002	0.002
923	0.041	0.042	0.006	0.012	0.004	0.004
1023	0.054	0.056	0.012	0.021	0.008	0.009
1123	0.061	0.062	0.018	0.025	0.013	0.013
1223	0.066	0.064	0.021	0.026	0.016	0.015

using standard numerical techniques for differential equations and matrix solvers for a system of simultaneous equations with constant heating rate conditions during carbonisation. The details of the numerical scheme are described in the literature [23,24]. After acquisition and preliminary processing of the input data for the given Indian coals used in Tata Steel, the code calculates the yields of primary, secondary volatile matter and cumulative yield and composition of volatile matter and ultimate analysis of semi-coke at

specified temperature during carbonisation. The code then enters an iterative loop in which the temperature is increased from 623 K in the steps as specified by the user. At each stage of the iteration, the masses in primary volatile matter and the cumulative yields of the three secondary volatile matter species are revised.

The semi-coke yield and composition are calculated by mass balance on the five elements present and used to predict the mean relative atomic mass of semi-coke.

4. RESULTS AND DISCUSSION

The predicted primary and secondary volatile matter yields (*daf* initial coal basis) are shown in Figs. 4 and 5 respectively for coal A. The predicted total yield of volatile matter (at 3 K / min) and experimental data generated by Thermo-Gravimetric Analysis (TGA) is shown in Fig. 6. The evolution of primary volatile matter appears to be complete by 873 K, although the secondary volatile matter species continue to be released at 1273 K. The total volatile matter yield as a function of charge temperature has been validated with the Thermo-Gravimetric Analysis (TGA) experiment. Fig. 7 shows the variation of carbon and hydrogen and Fig. 8 shows variation of oxygen, nitrogen and sulphur content of the charge as a function of charge temperature during the carbonising cycle. The predicted pattern of the total volatile matter release is in good general agreement with that observed experimentally by TGA. In particular, the model reproduces the rapid evolution of primary volatile matter between 673 K and 773 K. Fig. 9 shows the variation of mean relative atomic mass for semi-coke composition during carbonisation. For Indian coal B, the predicted total yield of volatile matter (at 3K / min) is shown in Fig. 10. The variation of composition of the charge in terms of carbon, hydrogen, oxygen, nitrogen and sulphur as a function of temperature is shown in Fig. 11 and Fig. 12. In order to confirm the validity of the results obtained from the mathematical model, the results have been compared with the published data in literature /1,7,14/ and are found to be in good agreement (deviations are <5%). The broad trend of experimental cumulative yields /1,7,14/ of some of the volatile matter species depicted in table 4 pertaining to British coals are of very close resemblance with the model predictions shown in Fig. 5. The validity of an *ab initio* modelling approach is thus established from this observation. In all cases the evolution of primary volatile matter appears to be complete by 873 K, although the secondary is volatile. Fig. 13 shows the variation of mean relative atomic mass for semi-coke composition during carbonisation for coal B. In the predictions of the semi-coke composition at intermediate temperatures, the model consistently underestimates the oxygen content and overestimates the carbon content in comparison to other

studies /1,10,11/.

The mean relative atomic mass (in Figures 9 and 13) for semi-coke is calculated by the following formula.

$$\frac{1}{A} = \frac{C}{12} + H + \frac{O}{16} + \frac{N}{14} + \frac{S}{32} \quad (13)$$

where A is mean relative atomic mass and C, H, O, N and S are atomic masses of carbon, hydrogen, oxygen, nitrogen and sulphur respectively.

The predicted variation of the final yields of the main hydrogen containing species with coal type is consistent with the preferential loss during coalification of those species having the lowest activation energy. As the hydrogen content of the coal is reduced during coalification, it is the yield of the tar, which falls, rather than the yields of CH₄ or H₂. The model takes into account the kinetics of primary volatile matter release. Because of the wide range of temperatures over which secondary volatile matter release occurs, the evolution of these species is not described kinetically in the present model. The evolution of three secondary volatile a matter species (CH₄, H₂, CO) occurs simultaneously. Although each may be the final product of a complex sequence of reactions, it is assumed in the model that their evolution can be considered independently.

5. CONCLUSION

A mathematical model of volatile matter release is proposed and parameters of the model have been generated from the literature information. The yield and composition of the volatile matter was predicted as a function of temperature from the ultimate analysis of the Indian coals and the heating profile. The model considers the evolution of the species, namely, primary volatile matter, methane, carbon monoxide and hydrogen. The evolution of these species is governed by parallel first-order decomposition reaction, the rate constant for which depends on a distribution of activation energies. The final yields of the species and composition of the charge are estimated from the ultimate analysis of the coal and heating profile using the concepts of rate phenomena. The predictions of the model and their broad trends are in good agreement with the TGA experimental data. The predictions of the

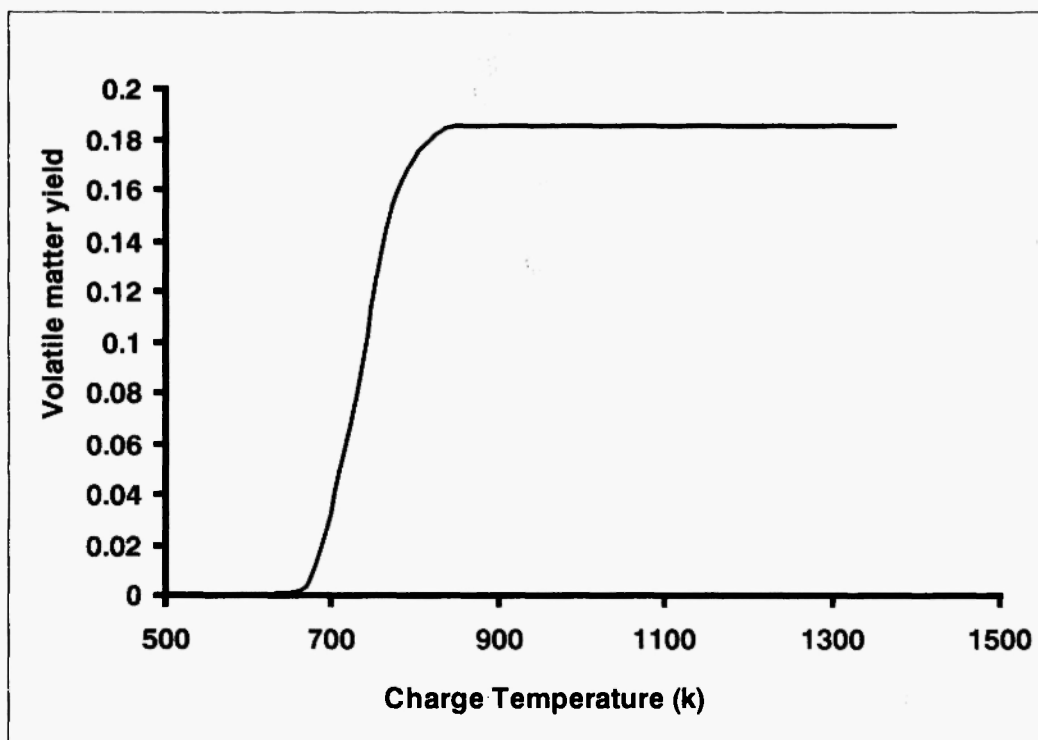


Fig.4: Predicted primary volatile matter yield (Indian coal A)

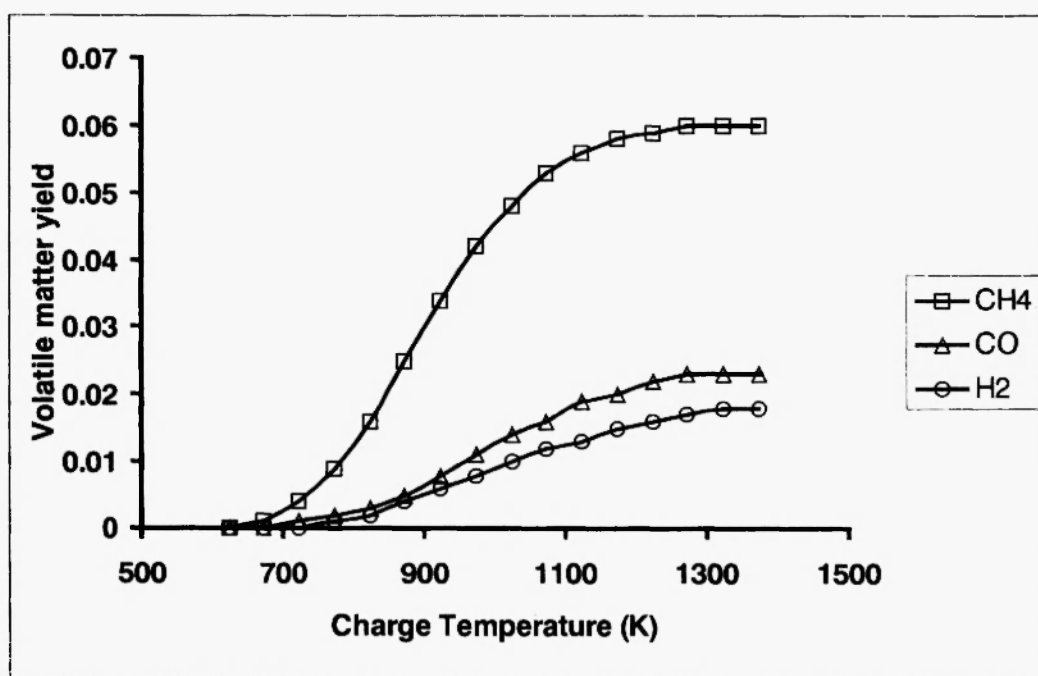


Fig. 5: Predicted secondary volatile matter yield (Indian coal B)

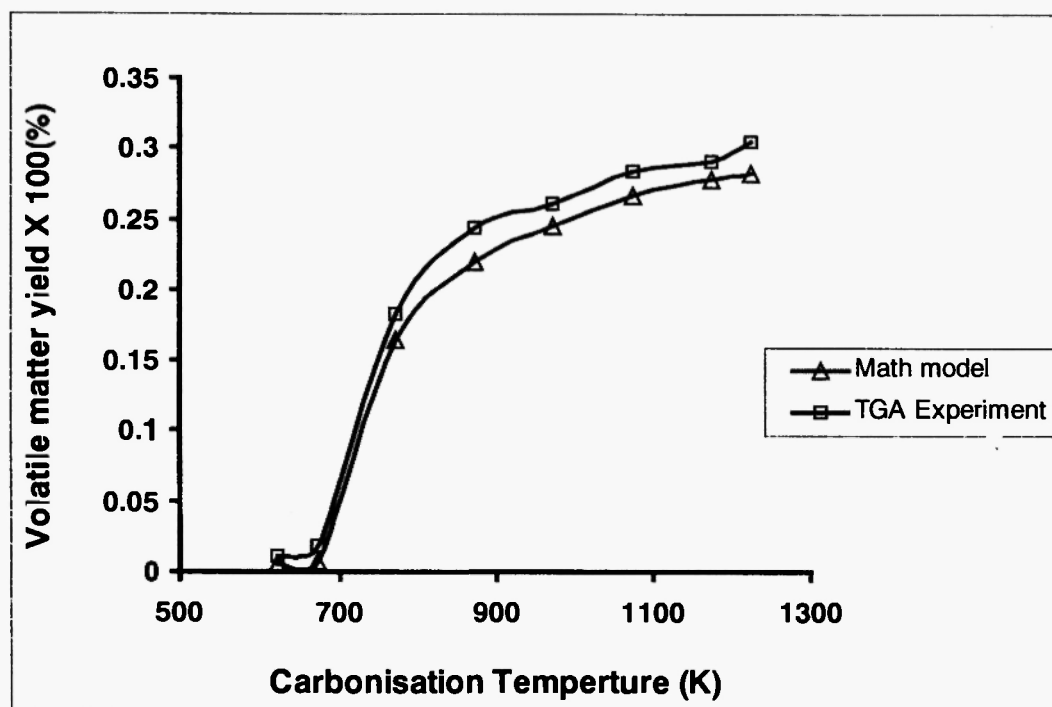


Fig. 6: Predicted total volatile matter yield (Indian coal A)

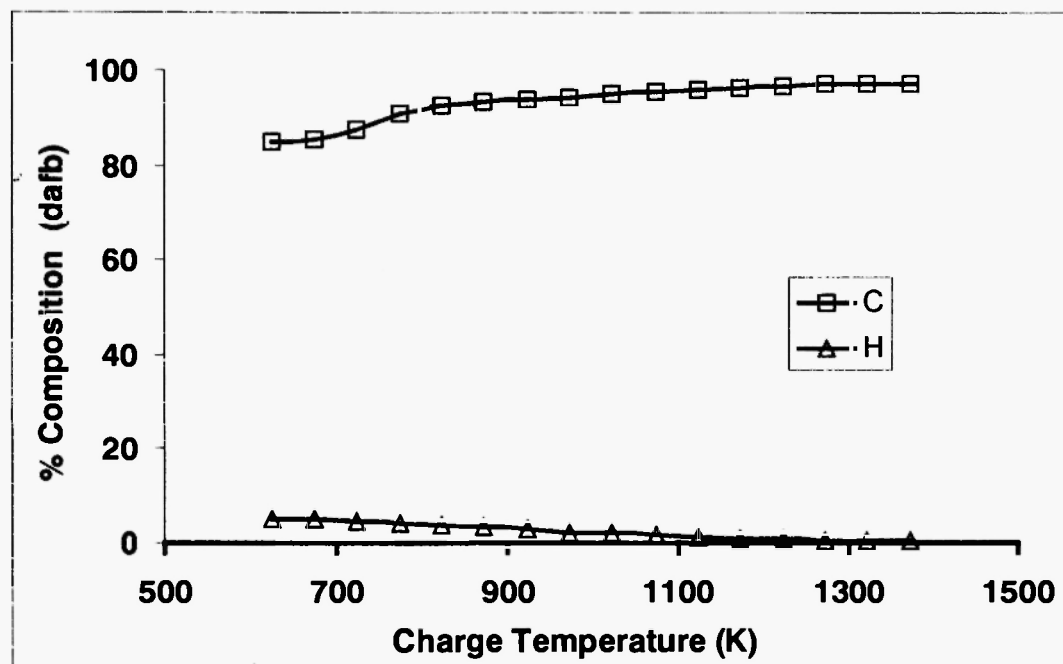


Fig.7: Variation of charge composition with temperature (Indian coal A)

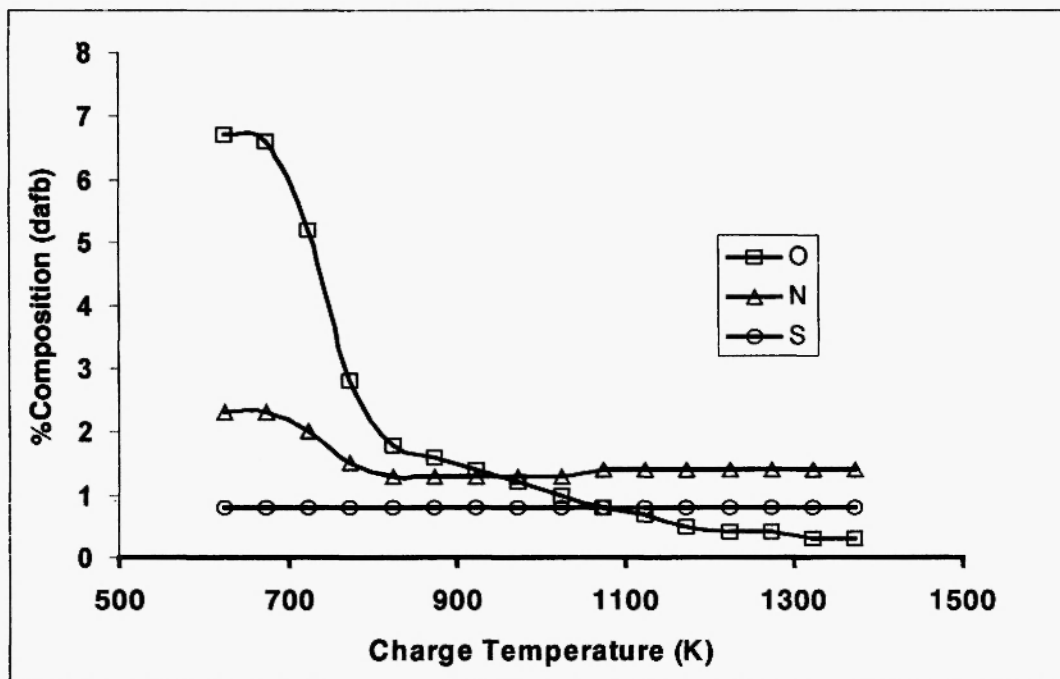


Fig. 8: Variation of charge composition with temperature (Indian coal A)

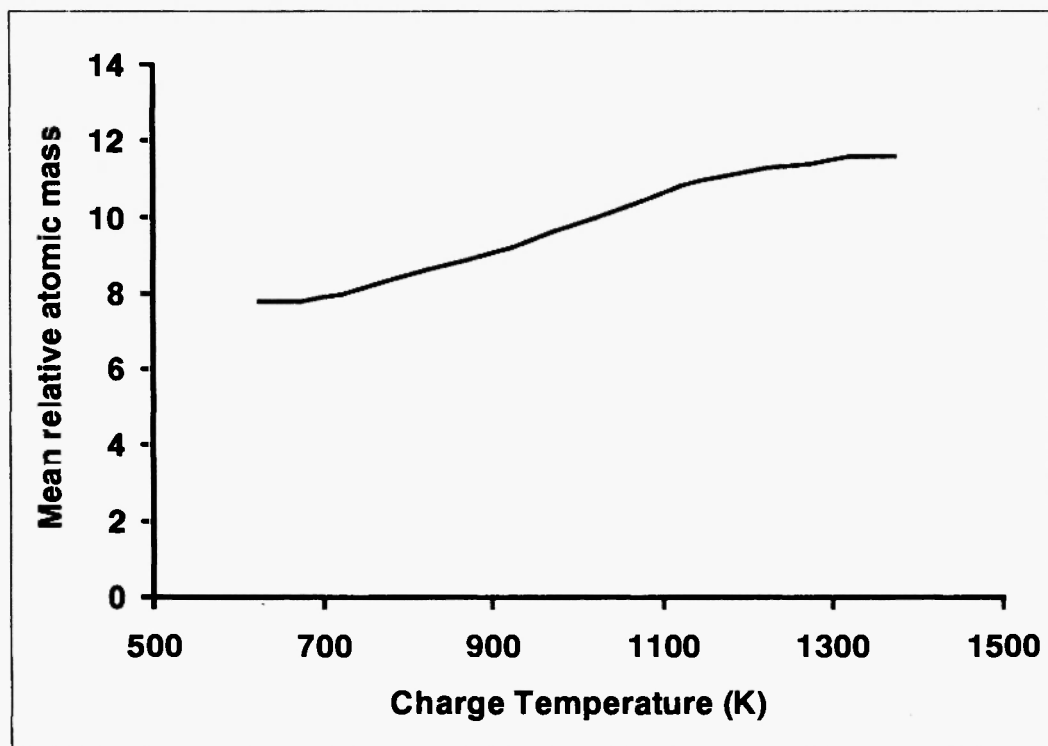


Fig. 9: Variation of semi-coke composition (Indian coal A)

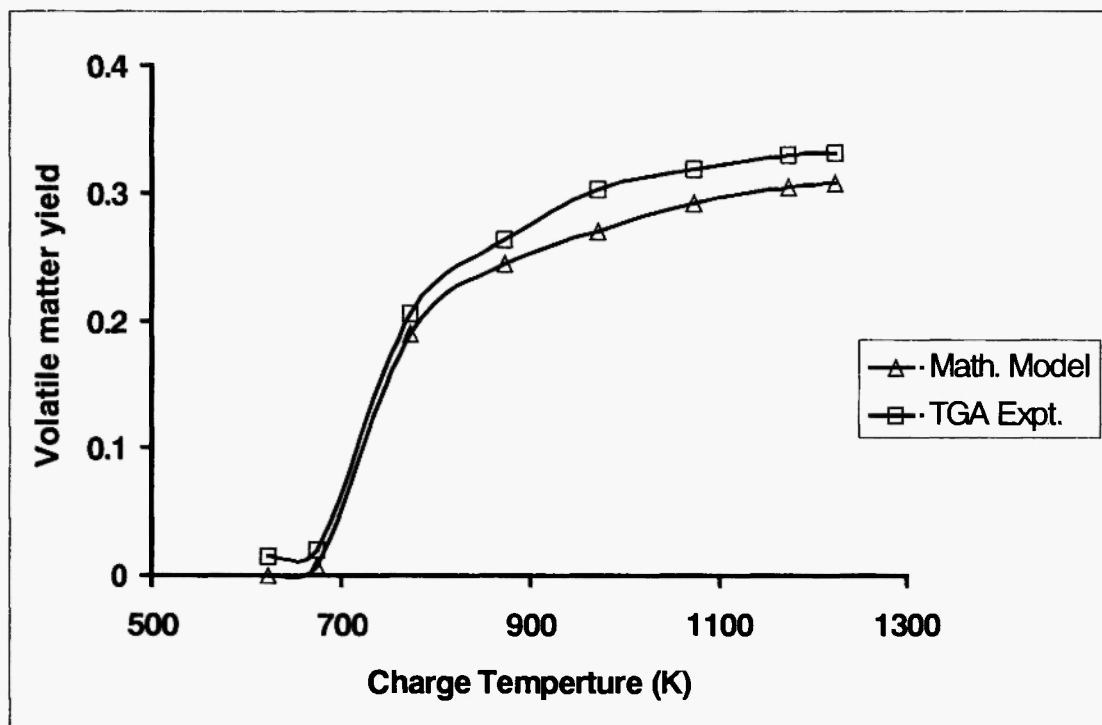


Fig. 10: Predicted total volatile matter yield (Indian coal B)

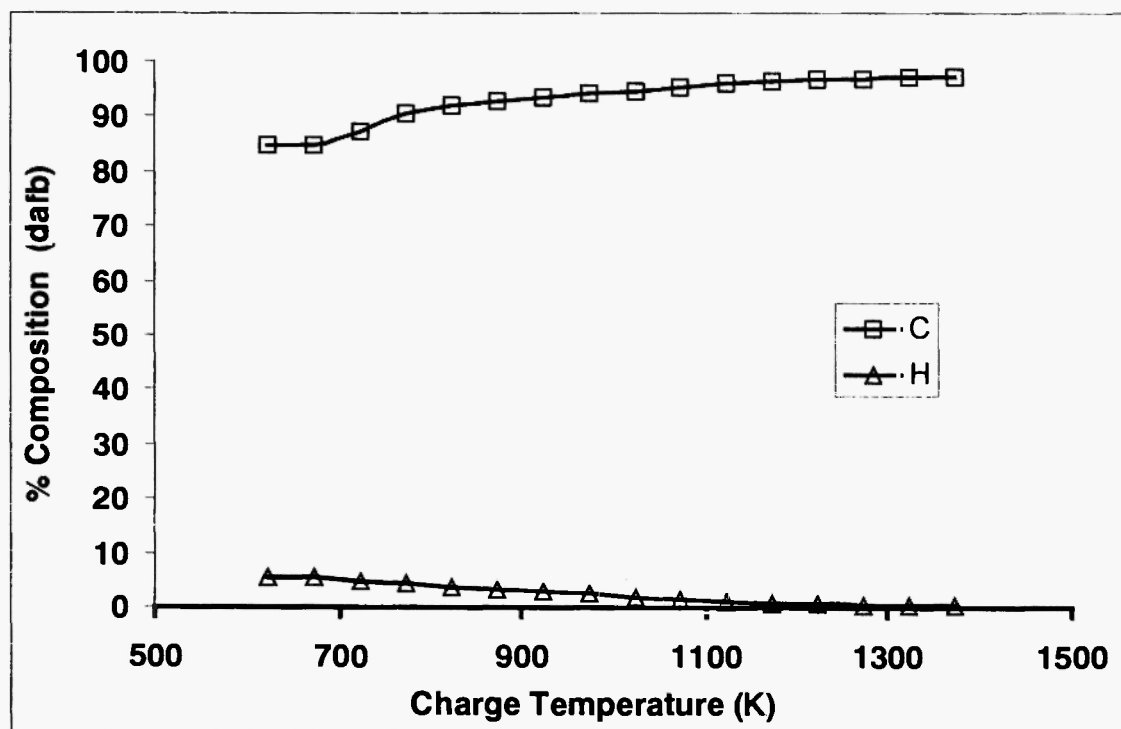


Fig. 11: Variation of charge composition with temperature (Indian coal B)

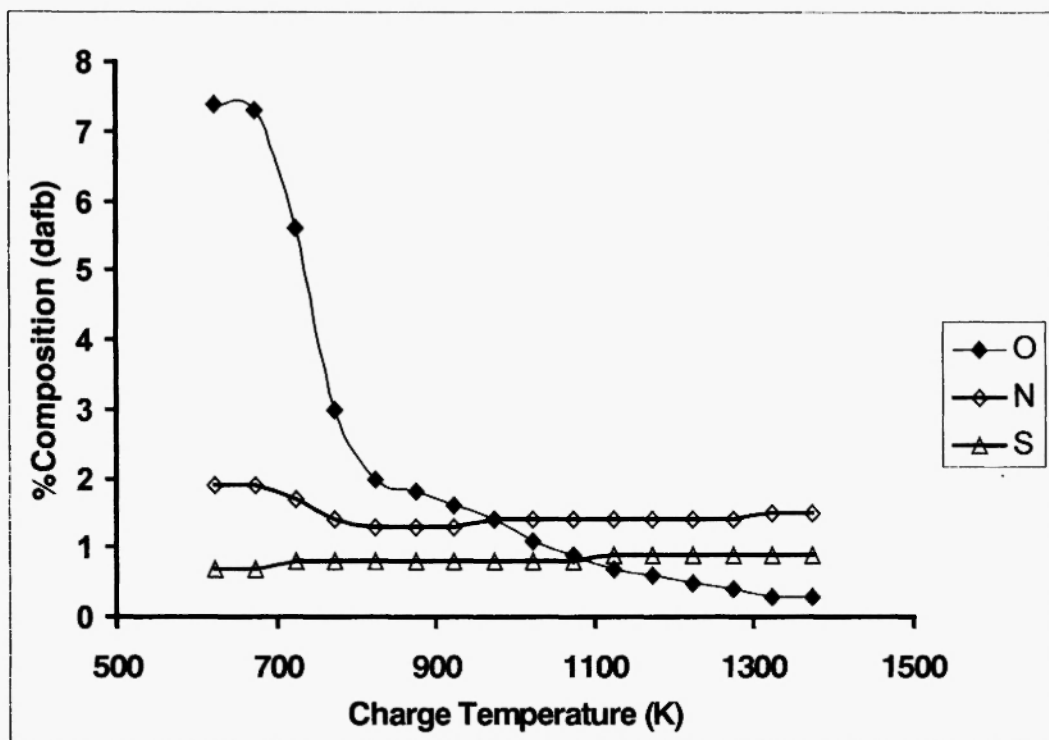


Fig. 12: Variation of charge composition with temperature (Indian coal B)

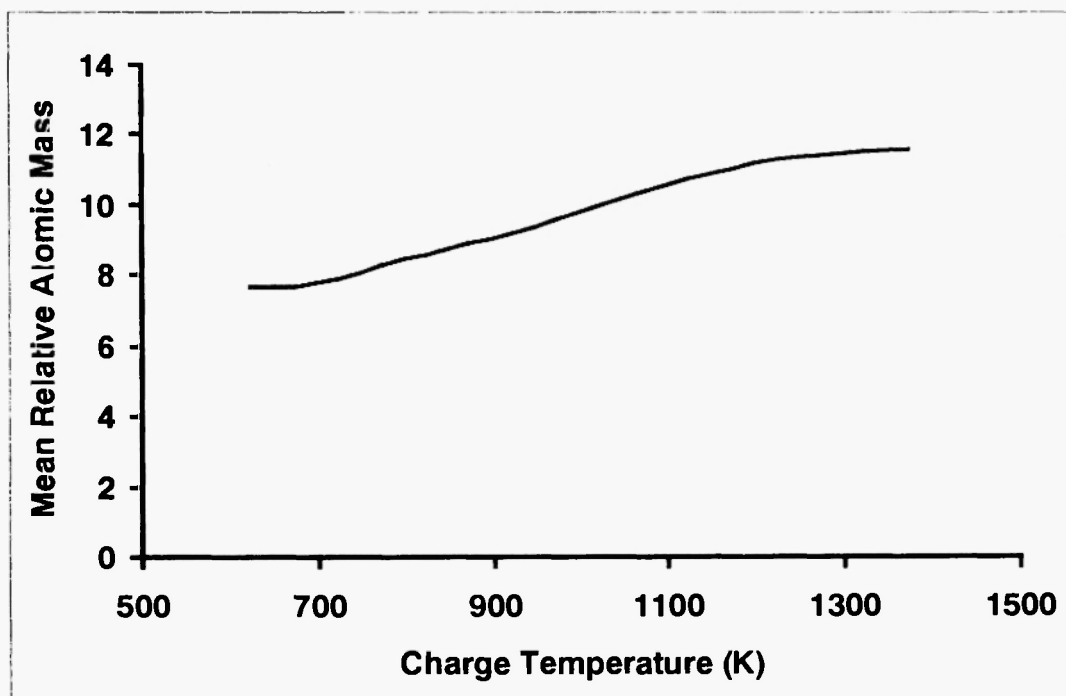


Fig. 13: Variation of semi-coke composition with temperature (Indian coal B)

model reproduce the main trends of volatile matter evolution with the given rate of heating and coal types in the previous studies. However, the main source of uncertainty in some of the predictions is attributed to lack of availability of extensive database for Indian coals.

NOMENCLATURE:

- A = constant which indicate the number of equations
 b = ultimate analysis of *daf* coal
 E = activation energy of volatile matter species
 k = frequency factor
 m = final yields as mass fractions of *daf* coal
 R = universal gas constant
 T = temperature in K
 y = total yields of volatile matter species
 α = constant which varies both with the species and rank of coal
 β = constant which varies both with the species and rank of coal
 δ = fraction of the component of volatile matter released in time t

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