

A COALIFICATION MODEL

Herman P. Ruyter

KONINKLIJKE/SHELL-LABORATORIUM, AMSTERDAM
(Shell Research B.V.)

P.O. Box 3003, 1003 AA AMSTERDAM, the Netherlands

Abstract

A series of low-rank materials, ranging from biomass waste to subbituminous coal, have been subjected to hydrothermal coalification, i.e. heat treatment in an autoclave with water. The results, together with relevant literature data, cover a wide field of reaction conditions: temperatures from 120 to 390 °C and residence periods from 1 minute to six months.

Using overall kinetics, the progress of hydrothermal coalification in terms of the evolution of carbon dioxide as a function of the conditions has been expressed in a simple model. Low rank materials can be described in terms of properties that can be gathered into general relationships which hold over wide ranges. Over the range from biomass to subbituminous coal, where coalification mainly implies the evolution of water and carbon dioxide, the conversion model allows the prediction of the enrichment of a material on the basis of feedstock properties and the conditions applied.

1. INTRODUCTION

Coal genesis, the transformation from plant waste to black coal, is governed by large numbers of processes of polymerization, degradation and coalification. The study of coal genesis has a long history. Experiments imitating coalification by subjecting a material to heating with water under pressure were first reported by Bergius (1) in 1913. He called it hydrothermal carbonization and produced a black product and defined the type of reaction to be only valid up to a certain degree of coalification ("Endkohle").

Bergius' story was amended later by various researchers. Thus, van Krevelen (2,3) proved that plant species of a certain nature could give specific recognizable lithotypes in the coal product and that the medium affects the result. Kreulen (4,5) showed that instead of one reaction, several chains of chemical reactions are involved, with their own intermediate products. Moreover, he found that the carbon dioxide quantity evolved exceeded by far the amount predictable on the basis of the carboxylate content of the feed, on the basis of which he stated that there was more than only decarboxylation. Leibniz (6) found the importance of H₂O (either steam or water) for the mechanism of the reaction. Compared with pressurized steam heating over the same time intervals, dry heating gave hardly any result. Terres (7) proposed to use and manipulate this process for upgrading and for achieving a better coking performance of the product. Gillet (8) summarized the state of the art and made an attempt at generalization, which, it should be added was not too successful due to the excessive number of variables.

Summarizing, we may say that up to the stage of subbituminous coals, plant materials in a wet medium can degrade to evolve mainly CO₂ and H₂O. The process has been looked at frequently, at least in a qualitative way. Quantification has been scarce. This may be due to the absence of single pure compounds and proper single chemical reactions, making it virtually impossible to establish a mechanism as a basis for kinetic measurement and calculations.

As a by-pass we have now replaced the chemistry by a macro approach. We found that for the saturated steam treatment, within certain limits, a few factors may be assumed constant. One of these is the molar ratio of CO₂ to H₂O formed, which gives a link to the C-H-O relation and the gross "chemical reaction". This allows a description of the "conversion" in terms of the change in oxygen content of a material.

We derived general relationships between some fuel properties over the relevant range of materials, which can be expressed in terms of the oxygen content as well. With these relations, the change of properties can be predicted along the coalification path.

2. RELATIONS BETWEEN PROPERTIES FOR BIOMASS, PEAT, BROWN COAL AND SUBBITUMINOUS COAL

Low rank materials (LRM) are here taken to mean materials formed by photosynthesis, which by a variety of processes, eventually turn into black coal. The variety of products is infinite and the complexity of the individual mechanisms far from understood. Yet, some of the properties of importance in connection with the use of the material as a fuel show coherent trends. This is indicated in Table I.

TABLE I
PRODUCT PROPERTIES AND THEIR VALUES IN THE RANGE
FOR WHICH CORRELATIONS ARE DERIVED

Property	Unit	Symbol	Total range biomass-subbitum. coal
water content	%w as received (AR)		90 - 9
" "	kg H ₂ O/kg DAF material	MC	10 - 0.1
calorific value	dry ash free base MJ/kg	CV _{DAF}	15 - 32
" "	wet " " " "	CV _{AF}	1.5 - 30
gross weight	dry " " " kg/GJ	GW _{DAF}	75 - 30
" "	wet " " " "	GW _{AF}	600 - 30
carbon content	%w dry ash free	C	40 - 80
oxygen content	" " " "	O	50 - 6
atomic ratio		OCR	1.0 - 0.06
oxygen/carbon			

The wide scatter of data on LRM properties can, to start with, be reduced significantly by recalculation on a new basis, viz. the mineral-matter (or ash)-free organic fraction, be it wet (AF) or dry (DAF). The moisture content itself (MC) is calculated as the weight of water per kilogram dry organic material.

Below we set up quantitative relations between the chemical composition, the calorific value and the moisture-binding tendency of LRM. The key to the relations is the oxygen content. The oxygen-containing groups give polarity to the carbon chain backbone of LRM. This determines the hydrophobicity of a material.

The calorific value (CV) of wet material depends on the MC and the CV of the dry material. We assume these to be dependent on the chemical composition, which is not a random distribution. In particular, the oxygen and carbon content of LRM move along natural degradation routes. In a first approximation we assume the sum of the percentages of oxygen and carbon to be constant (Σ). We define OCR as the atomic ratio of oxygen to carbon in the dry organic fraction:

$$\text{OCR} = \frac{\% \text{ oxygen}/16}{\% \text{ carbon}/12} = \frac{\% \text{O}}{\% \text{C}} \times 0.75, \quad 1)$$

with the constant sum, Σ , given by:

$$\text{OCR} = \frac{0.75 \Sigma}{\% \text{C}} - 0.75.$$

In Fig. 1 we plotted OCR against the reciprocal of the carbon content for a set of materials ranging in quality from biomass to subbituminous coal. From the figure we read:

$$\text{OCR} = \frac{68}{\% \text{C}} - 0.75. \quad 2)$$

For the calculation of the calorific value of a coal on the basis of its major constituents many formulas can be found in the literature. For low-sulphur materials the following is one of the simplest.

$$\text{CV}_{\text{DAF}} = 0.34 (\% \text{C}) + 1.40 (\% \text{H}) - 0.16 (\% \text{O}), \text{ MJ/kg}. \quad 3)$$

In Figure 2 it is shown how this formula approximates the calorific value of our low-rank materials.

The relation between MC and OCR has been established in Fig. 3. From this figure we get

$$\text{OCR} = 0.31 (\text{BMC})^{0.49} \quad 4)$$

where BMC is the inherent bed moisture content.

The hydrogen content varies from 6 % for biomass, to 3 $\frac{1}{2}$ % for subbituminous coal. If we assume linearity for the relation between hydrogen content and OCR, and substitute equation 2 into equation 3, we get approximately

$$\text{CV}_{\text{DAF}} = \frac{30 - 5 \text{OCR}}{0.75 + \text{OCR}}. \quad 5)$$

When we substitute (4) into (5), we arrive at the actual measured variables MC and CV,

$$\text{CV}_{\text{DAF}} = \frac{30 - 1.55 \text{BMC}^{0.49}}{0.75 + 0.31 \text{BMC}^{0.49}} \quad 6a)$$

and

$$CV_{AF} = CV_{DAF} \cdot \frac{1}{BMC + 1}$$

6b)

These lines are depicted in Fig. 4. The scatter of the measured data is small. This may be explained by the fact that deviations for the CV and the OCR occur on the same material in the same direction, and thus compensate each other. It should be pointed out, however, that the largest deviations occur with high contents of mineral matter. Apart from the calculation error, probably the contribution of minerals to the water absorbency etc. cannot be completely ignored.

The above set of relations was obtained from only limited numbers of data and deals with few properties. Still, it may be used as a basis for more sophisticated work on more specific groups of materials.

3. HYDROTHERMAL COALIFICATION EXPERIMENTS

From the wide variety of experimental results available both from our own work and the literature, we selected those of a number of constant-volume batch experiments, with variation of feedstock, temperature and time only. The pressure was always approximately the vapour pressure of saturated steam at the temperature chosen.

In the KSLA programme per experiment 50 grams of wet feed material and 30 grams of demineralized water were heated in an autoclave by electric heating from outside. In a systematic series of experiments carried out on two brown coals with moisture contents of 35 and 60 %w respectively, the temperature was varied between 175 °C and 350 °C and the residence time at the maximum temperature from one minute to three hours. After cooling, the gas volume was measured and analysed and the coal product weighed and analysed to complete the balance. In addition, a variety of feed materials ranging in rank from cellulose to subbituminous coal were tested under the low and the high temperature conditions.

The use of pressure resistant autoclave walls implies that the reported reaction times at a certain temperature should be corrected for the inertia of the metal mass. The effect becomes less important for longer experiments. In the KSLA experiments the temperature at the centre of the sample increased at a rate of approx. 6 °C/min. This means that a "zero" residence time at 340 °C includes 15 min at 300 °C, 30 min at 250 °C or 45 min at 200 °C.

Various series of similar experiments under different conditions and using a wide variety of feedstocks were reported by Van Krevelen (3). He used 20 grams of material per experiment and varied the temperature from 225 °C to 390 °C and the residence time from 3 to 72 hours.

Kreulen (5) reports series of experiments of longer duration: 200-3200 hours, i.e. almost six months. He used pressure resistant glass tubes, which were welded after being filled with half a gram of sample. The tubes were heated together in a hot air stove at temperatures varying from 130 °C to 180 °C. After certain time intervals, tubes were taken out, cooled, opened and the contents analysed.

4. MODEL FOR (HYDROTHERMAL) COALIFICATION

The application of basic kinetics to the experimental results requires some manipulations. We want to use (9):

$$\text{reaction rate} = -\frac{dc}{dt} = -K_T F(c^n) \quad (8)$$

(c = concentration, n = order of the reaction)

$$\text{and Arrhenius } K_T = K_0 \cdot e^{-\frac{E_A}{RT}} \quad (9)$$

(E_A = activation energy)

Therefore, we take for the variable reflecting the concentration the oxygen content, and we define as "complete" conversion the reduction of the oxygen content to the level of subbituminous coal (ca. 6 %w DAF). O_{\max} becomes the difference in oxygen content between the feed and subbituminous coal. 0 is the figure for the percentage on dry ash free basis.

We found that the ratio at which CO_2 and H_2O was formed in the autoclave experiments was almost constant during heat treatment up to temperatures of about 350 °C and a conversion that reduces the oxygen content to nearly 10 %w, as is illustrated in Figure 5. The same was reported by Schafer (10) for low-temperature carbonization experiments in an ambient inert atmosphere up to a temperature of 400 °C.

$$\text{ratio } r = \frac{\text{mol } CO_2}{\text{mol } H_2O} = \frac{18}{44} \frac{\text{weight } CO_2}{\text{weight } H_2O} \quad (10)$$

This gives us linearity for the relation between the oxygen content and the CO_2 production, which is a convenient tool because the evolution of CO_2 is a parameter that is much easier to measure at intermediate stages. The ratio was found to vary with the type of feedstock, the pressure applied and the pH of the reaction medium. Assuming that all of the oxygen removed from the feed is converted to CO_2 and H_2O in a ratio r, it can be derived that:

$$CO_{2\max} = \frac{44}{32r + 16} \Delta O_{\max} \quad (11)$$

The conversion f of (hydrothermal) coalification at a certain time t becomes:

$$f = \frac{O_{\text{feed}} - O_t}{\Delta O_{\max}} = \frac{CO_{2t}}{CO_{2\max}} = CO_{2t} \left(\frac{32r + 16}{44r} \right) \left(\frac{1}{O_{F-6}} \right) \quad (12)$$

Here CO_2 is the amount expressed as the percentage of the dry ash-free base intake.

The conversion is obtained from equation 8 by integration to a certain point in time. A general solution is given by the Seitz Balazs equation (11).

$$\ln \frac{x_2}{x_1} = A \ln \frac{t_1}{t_2} + B \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (13)$$

This time-temperature equivalence predicts a relationship between time and temperature required to achieve a certain conversion:

$$t_1, t_2 = e^{\frac{A}{B} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)} \quad (f = \text{constant}) \quad (14)$$

The physical meaning of this is that the same amount of CO₂ could be measured after treatments in different ways: a short time at a high temperature or a longer period at a lower temperature.

In Figure 6, a graph of the logarithm of the time and the reciprocal temperature, we have plotted all the data of the three studies recalculated to the conversion *f* with equation 12, and rounded off to 0.1, 0.2 etc. Now we can read the coefficients for formula 13 from the graphs of the pairs of parameters separately. We obtain approximately:

$$f = 50 t_s^{0.2} e^{-\frac{3500}{T_K}} \quad (15)$$

Although this formula cannot be considered proper chemical reaction kinetics because neither the reagent nor the reaction itself is defined, we still tried an extrapolation. Of course the integration (the basis for *f*) is impossible to perform in the natural case since the data on the history are lacking. However, the ages of various products fortunately are quite well known. If we then assume biomass with ca. 50 %w oxygen to have been the feedstock, we get for the conversion *f*, values of 0.15 for humus, 0.30 for peat, 0.50 for brown coal and more than 0.8 for coal. Substitution in equation 15 yields a temperature for each material. An essentially constant value is obtained for time scales from 10³ to 10⁸ years, i.e. about 40 °C, which is in line with the probable historical average.

5. APPLICATION TO THE QUANTIFICATION OF UPGRADING

The removal of H₂O and CO₂ results in enrichment of the material as a fuel, i.e. the same heating value is concentrated in a smaller weight. The enrichment forms a necessary step in the upgrading of a fuel. This enrichment starts with dewatering (Fleissner) (12). The dewatering will not proceed to complete dryness, because the LRM will retain or reabsorb water to a certain level of equilibrium with the surrounding atmosphere. For further enrichment the rank has to be changed by also removing (polar) oxygen by decarboxylation and dehydration, to maximum drying at the level of subbituminous coal. Further coal rank improvement takes place via other mechanisms (demethanization).

In upgrading we look at properties such as moisture content and calorific value rather than the molecular composition. The transformation can be carried out with the use of the relations derived in section 2. We can define another conversion factor *f'*:

$$f' = \frac{OCR_{feed} - OCR_t}{\Delta OCR_{max}} \quad 16)$$

with the limitation $\Delta OCR_{max} = OCR_{feed} - OCR_{subbituminous\ coal}$
 $= OCR_{feed} - 0.06$

We can express the "enrichability" or the prediction of product properties in terms of the OCR:

$$OCR_{product} = (1-f')(OCR_{feed}-0.06) + 0.06 \quad 17)$$

This can be substituted in the relations of section 2 and then we can calculate product properties on the basis of the feedstock analysis and the extent of conversion, which is measured by the amount of CO₂ evolved, as described in section 4. For instance by substitution of equation 17 in equation 5 the calorific value becomes

$$CV_{productDAF} = \frac{30 - 5 [(1-f')(OCR_{feed} - 0.06) + 0.06]}{0.75 + (1-f')(OCR_{feed} - 0.06) + 0.06} \quad 18)$$

with $OCR_{feed} = 0.31$ (bed moisture content)^{0.49}. This can be further substituted in

$$CV_{AF} = \frac{1}{1 + MC} CV_{DAF} \quad 18a)$$

(moisture content in kg H₂O/kg DAF, calorific value HHV in MJ/kg),

For practical reasons, in the further use of the relation to quantify the extent of enrichment of a material, we introduce an extra variable, the gross weight:

$$GW = \frac{1000}{CV} \text{ kg/GJ} \quad 19)$$

Finally, we define the enrichment of the LRM to a fuel as the factor E: the weight reduction per unit energy:

$$E = \frac{GW_{feed} - GW_{product}}{GW_{feed}} * 100 \% \quad 20)$$

or

$$E = \left[1 - \frac{1 + MC_{prod.}}{1 + MC_{feed}} \cdot \frac{CV_{feed}}{CV_{prod.}} \right] * 100 \%$$

which can by substitution of the previous be transformed to:

$$E = 1 - \frac{\left[1 + 5 \left\{ (1-f')(0.31(MC)^{0.49} - 0.06) \right\} \right] \left[\frac{30 - 1.55 (MC)^{0.49}}{0.75 + 0.31 (MC)^{0.49}} \right]}{\left[1 + MC \right] \left[\frac{30 - 5(1-f') \left\{ 0.31(MC)^{0.49} - 0.06 \right\}}{0.75 + (1-f') \left\{ 0.31(MC)^{0.49} - 0.06 \right\}} \right]} * 100 \% \quad 21)$$

where MC is the feed moisture content and f' the conversion, expressed in OCR.

Figure 7 shows the lines obtained when formula 21 is calculated as a function of feed moisture content and degree of conversion. It shows what improvement can be expected after hydrothermal coalification treatments at various conditions. We also plotted points measured in our experiments under mild and severe conditions. We varied the feedstock quality from biomass waste to subbituminous coal. It is clear that the relative effect of the treatment is larger for younger feed materials.

The circles in the figure connected with a dashed line show the range of results obtained with the 60 % moisture brown coal under the variety of conditions used in section 4.

REFERENCES

1. Bergius F., Die Anwendung hoher Drucke bei chemischen Vorgängen, Halle, 1913.
2. Van Krevelen D., Graphical statistical method for the study of structure and reaction processes of coal, Fuel, 1950, 29, No 12, 269.
3. Schuhmacher J. and van Krevelen D., Studies on artificial coalification, Fuel, 1960, 39, 223.
4. Kreulen D. and Kreulen van Selms F., Thermische Zersetzung von Lignin and Humin bei relativ niedrigen Temperaturen, Brennstoff Chemie, 1957, 38, p 49-54.
5. Kreulen D., Freiburger Forschungsheft 1962, A 244, p 46-59.
6. Leibniz E., Zur Kenntnis der Kruckinkohlung von Brannkohlen im Gegenwart von Wasser, Journal für praktische Chemie, 1958, 4. Reihe, Band 6, p 18-22.
7. Terres E. Über die Entwässerung und Veredlung von Rohtorf und Rohbraunkohle, Brennstoff-Chemie, 1952, 33, p 1-12.
8. Gilet A., Von der Zellulose zum Anthrazit, Brennstoff-Chemie, 1955, 36 p 103-120, 1956 37 p 395-401, 1957 38 p 42-50 p 151-160.
9. Levenspiel O., Chemical Reaction Engineering 1972, John Wiley & Sons Inc., New York, Chapter II.
10. Schafer H., Pyrolysis of brown coals. Fuel, 1979, 58 p 667-679.
11. Van Krevelen D., Properties of Polymers 1976, Elsevier Scientific Publishing Company, Amsterdam, p 292.
12. Fleissner H., Sparwirtschaft Wien, 1927, 10, p 500.

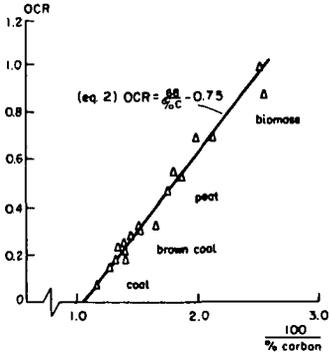


Fig. 1: Relation between oxygen/carbon ratio and reciprocal carbon

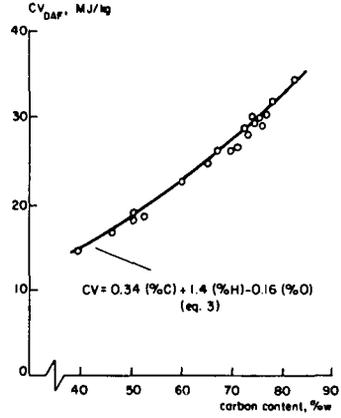


Fig. 2: Relation between calorific value and carbon content

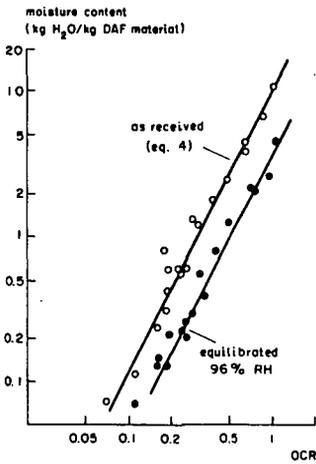


Fig. 3: Relation between moisture content and oxygen/carbon ratio

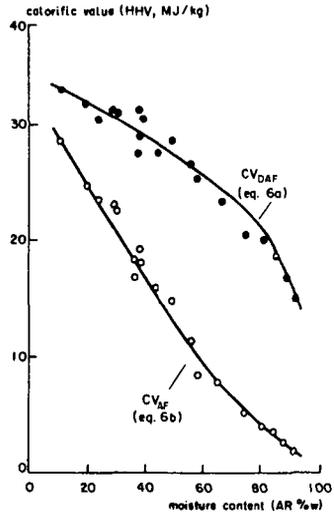


Fig. 4: Relation between calorific value and moisture content

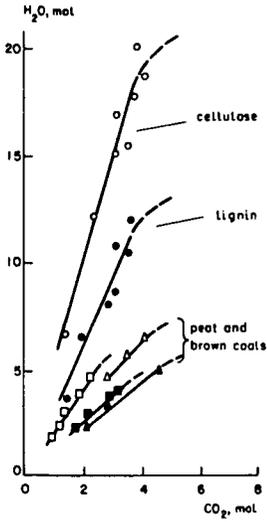


Fig. 5: Ratio between amounts of carbon dioxide and water evolved

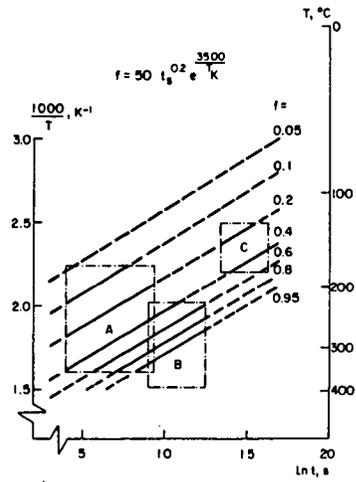


Fig. 6: Conversion (f) as a function of temperature (T) and time (t).
Boxes : experimental data A: KSLA, B: ref. 3, C: ref. 5

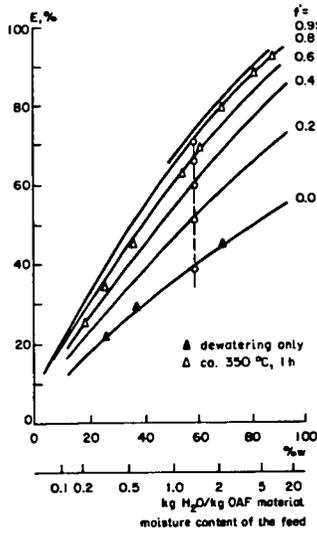


Fig. 7: enrichment as a function of conversion for various feedstock qualities