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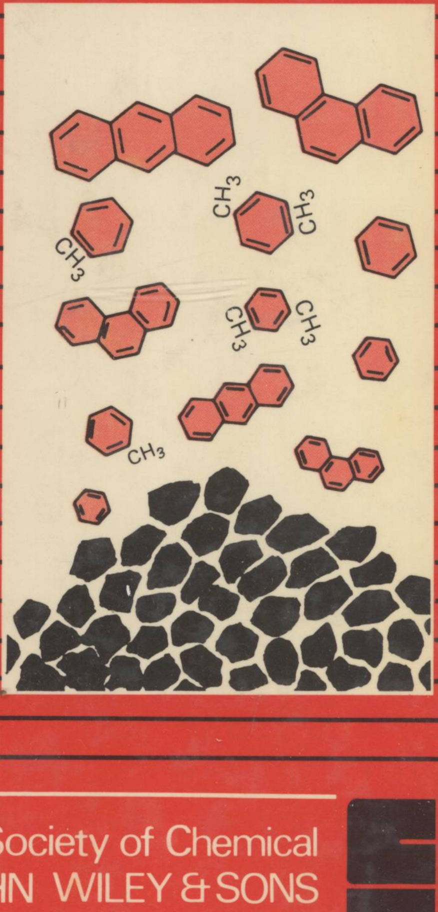
Chemicals from Coal: New Processes

Edited by K.R.PAYNE



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Chemicals from Coal: New Processes

Editor's introduction

The first volume on chemicals from coal (*Chemicals from Coal: New Developments, Critical Reports on Applied Chemistry, Volume 9*) included chapters on the overall economics of coal chemistry and recent technical advances in the pyrolysis and liquefaction of coal. The present volume completes this review of the production of coal-based chemicals with chapters on the gasification of coal, the Fischer–Tropsch process, and a study of the calcium carbide route to coal-derived chemicals.

Both the carbide process and the Fischer–Tropsch synthesis have been known and operated for many years. The Fischer–Tropsch process was originally developed in Germany by BASF before the First World War, and was improved over the years until, by the advent of World War II, it became an important source of chemicals and fuel for the Third Reich. After World War II, the emergence of cheap oil from the Middle East generally made coal-based processes uneconomic. The exception was in South Africa, where economic conditions favoured the development of coal-based chemistry, and the resulting Sasol operation is described in this volume by Dr M.E. Dry of Sasol Technology (Pty.) Ltd.

The original Fischer–Tropsch catalysts were cobalt catalysts operating in the vapour phase. Over the years, there has been much research into the use of alternative catalyst systems for the Fischer–Tropsch process, both in the liquid and vapour phases, for the conversion of CO/H_2 mixtures to economically important chemicals and incorporating high selectivities. The value of this research is not entirely limited to coal chemistry, and Professor Wender's chapter describes the work carried out in this field.

A chapter on carbide chemistry has been contributed by Dr Kampmann and Dr Portz of the Knapsack works of Hoechst AG where carbide chemistry has been worked for many years. Dr Boy Cornils, also of Hoechst, has contributed a chapter on coal gasification processes, and has also provided a view of future developments in this area of coal chemistry.

At the present time, with the price of oil falling and with significant supplies available for the next 30 years or so, there are strong economic arguments against the immediate and general use of coal as a source of chemical intermediates. In the longer term, however, the substantial supplies of coal available will guarantee its role as a source of energy and chemicals long after oil and gas have ceased to be available.

K.R. Payne

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1 Syngas via coal gasification

B. Cornils

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1 Introduction

Synthesis gas, the mixture of carbon monoxide and hydrogen, is an ideal connecting link between coal—as a source of fossil carbon—and chemicals. Figure 1.1 shows this in diagrammatic form.[1,2] According to route A, the coal is initially transformed into synthesis gas with the aid of gasification agents such as water and oxygen. The synthesis gas can then be converted by means of suitable synthesis processes into the desired intermediate products. As can be seen from Fig. 1.2, there is a large number of such synthetic processes available which permit the production of saturated hydrocarbons, olefins, alcohols, carboxylic acids or other oxygen-containing compounds as well as aromatic basic materials.[3] The primary products shown in Fig. 1.2 using synthesis gas as a chemical building block can in turn also be further processed in a wide variety of ways. Existing and potential synthesis gas applications are compiled in Fig. 1.3.[4]

Compared with the method via the carbide route and acetylene (route B in Fig. 1.1), the route via coal gasification and synthesis gas has fewer process stages, is technologically safer, and is also the most advanced from the engineering point of view. Route C in Fig. 1.1, on the other hand, has the same smaller number of steps on paper, but the coal hydrogenation process leads primarily to very complicated reaction mixtures including coal oils, which can only be separated into basic and intermediate products by relatively expensive refining processes. One look at the structure of coal (Fig. 1.4)[5] is enough to see that even mild hydrogenation after cracking of suitable C–C or C–hetero atom bonds mainly leads to product mixtures and not, as in the case of selective syntheses, to one final product. The apparent advantage of coal hydrogenation—the direct conversion

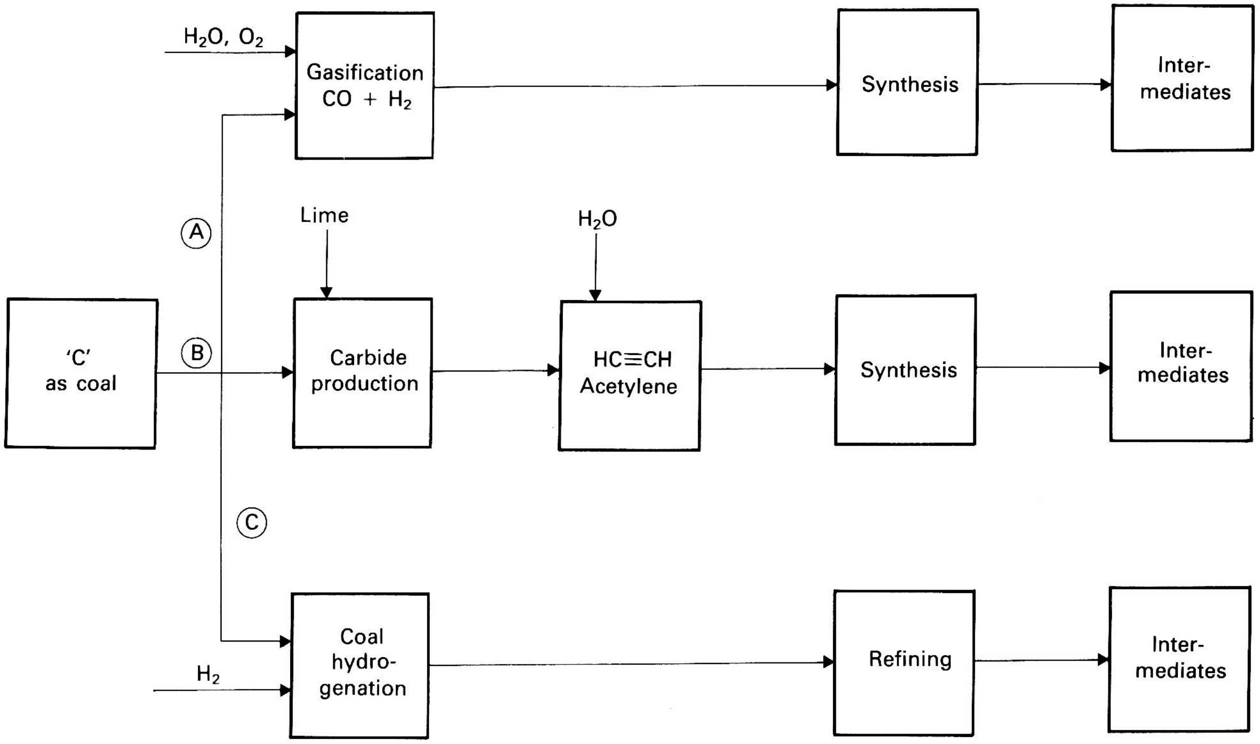

Fig. 1.1. Possibilities of a 'reconnection' between coal and chemicals.

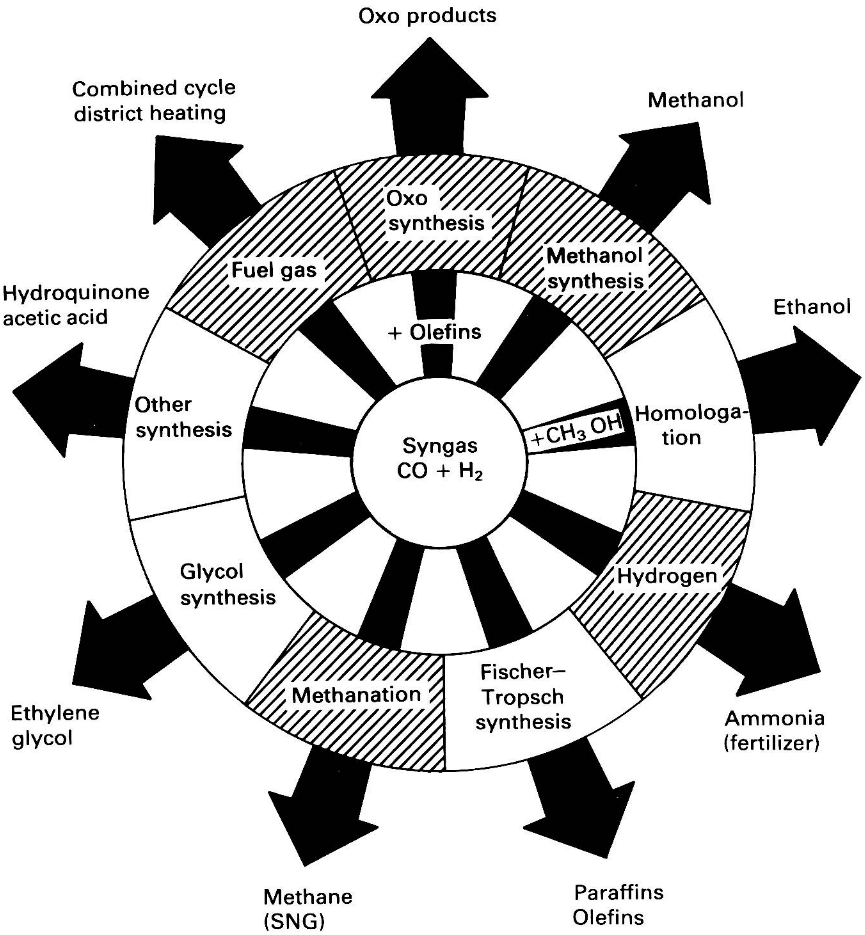

Fig. 1.2. Syngas as a building block.

of solid coal into liquid coal oils which are easy to handle—is therefore offset by the expenditure on special coal oil refineries which are only partly similar to the conventional refineries. This is where the significance of the route via synthesis gas lies, which, as a chemical entity, can be produced not only from coal but also from heavy fuel oil and natural gas and fed into existing process plants without further plant modifications.

A combination of routes A and C in Fig. 1.1 is possible in the form of integrated coal hydrogenation plants where gasification of the liquid residue of

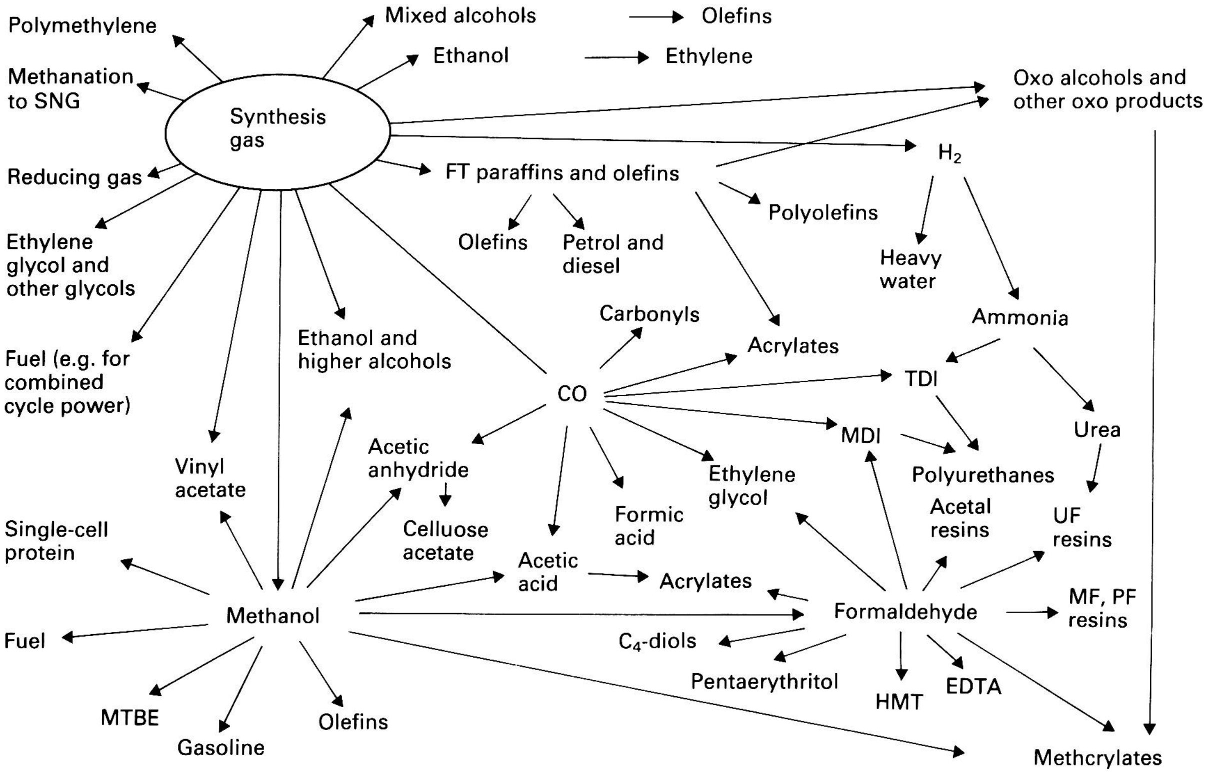

Fig. 1.3. Existing and potential synthesis gas applications (FT = Fischer–Tropsch; TDI = toluene diisocyanate; MDI = diphenylmethane diisocyanate; UF resins = urea formaldehyde resins; MF resins = melamine formaldehyde resins; PF resins = phenol formaldehyde resins; EDTA = ethylene diamine tetra-acetic acid; HMT = hexamethylene tetramine; and MTBE = methyl tertiary butyl ether).

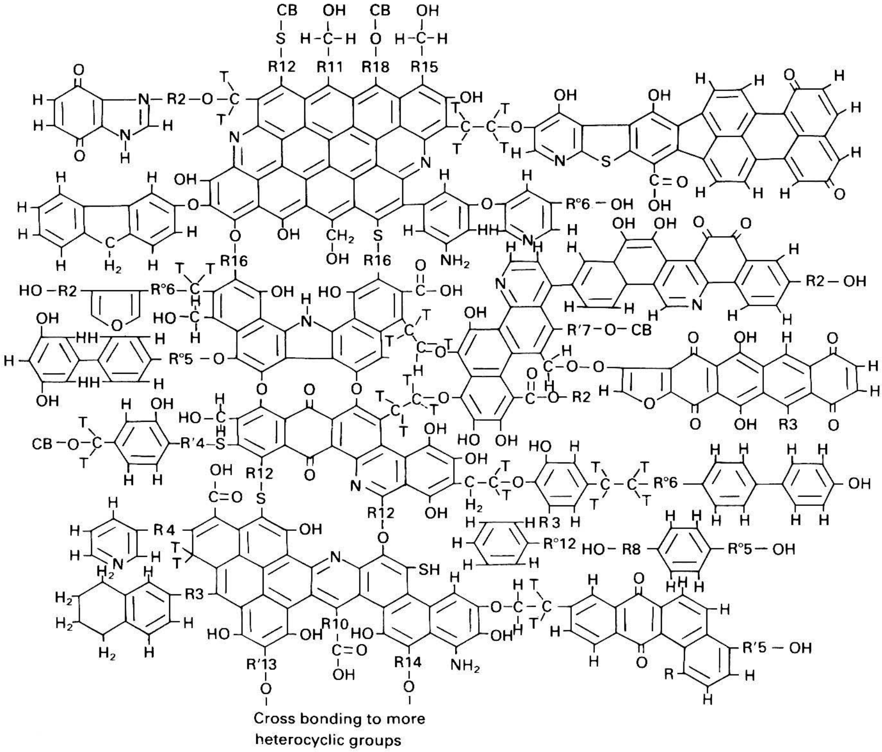

Fig. 1.4. Possible chemical structure of coal[5] (R°N = alicyclic rings of N carbons; RN = alkyl side chain of N carbons; R'N = unsaturated alkyl side chain of N carbons; CB = cross bonding by O or S to new heterocyclic groups with side chains; T = tetrahedral 3-dimensional C–C bonds, C–O bonds and C–S bonds).

coal oil distillation is located downstream of a coal hydrogenation plant.[6] Such an integrated hydrogenation/gasification plant produces coal oils which are further processed in the coal chemical refinery[7] as well as synthesis gas which can serve as a building block or, after conversion, as a source of hydrogen for the coal hydrogenation process itself (Fig. 1.5).

Producing chemicals from coal via the synthesis gas route, and so heralding the renaissance of coal chemistry, presupposes the availability of suitable gasification processes for the production of syngas from coal, i.e. its conversion, with the aid of the gasification agents, oxygen (air), steam, carbon dioxide or hydrogen or their mixtures, to combustible gases. Apart from the various development 'generations' of coal gasification processes, usually differentiated by the level of technology achieved, there is a basic difference between autothermic and allothermic coal gasification. The basis for this differentiation is the overall energy balance of the reactions involved in coal gasification, which are listed in Table 1.1.

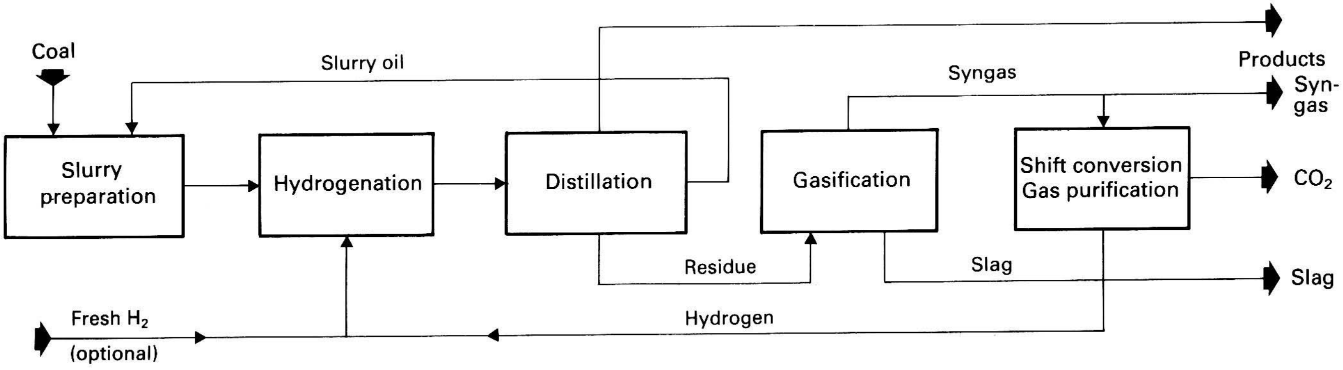

Fig. 1.5. Integrated coal hydrogenation plant.

Table 1.1 Reaction enthalpies and equilibrium constants of coal gasification reactions[8]

Reaction equation	Reaction enthalpy ΔH_R (kJ/mol)	Equilibrium constants		at 800°C	at 1300°C
1. $C+O_2 \rightleftharpoons CO_2$	−406.4	p_{CO_2}/p_{O_2}		$1.8\cdot10^{17}$	$1.5\cdot10^{13}$
2. $2\,C+O_2 \rightleftharpoons 2\,CO$	−246.3	$p^2_{CO_2}/p_{O_2}$	(bar)	$1.4\cdot10^{18}$	$4.5\cdot10^{16}$
3. $C+CO_2 \rightleftharpoons 2\,CO$	+160.8	p^2_{CO}/p_{CO_2}	(bar)	7.65	$3.00\cdot10^{3}$
4. $C+H_2O \rightleftharpoons CO+H_2$	+118.5	$p_{CO}p_{H_2}/p_{H_2O}$	(bar)	7.97	$9.98\cdot10^{2}$
5. $C+2\,H_2O \rightleftharpoons CO_2+2\,H_2$	+ 16.2	$p_{CO_2}p^2_{H_2}/p^2_{H_2O}$	(bar)	8.31	$3.32\cdot10^{2}$
6. $C+2\,H_2 \rightleftharpoons CH_4$	− 83.8	$p_{CH_4}/p^2_{H_2}$	(bar^{-1})	$4.72\cdot10^{-2}$	$1.82\cdot10^{-3}$
7. $2\,CO+O_2 \rightleftharpoons 2\,CO_2$	−567.3	$p^2_{CO_2}/p^2_{CO}p_{O_2}$	(bar^{-1})	$2.4\cdot10^{14}$	$5.0\cdot10^{9}$
8. $2\,H_2+O_2 \rightleftharpoons 2\,H_2O$	−482.1	$p^2_{H_2O}/p^2_{H_2}p_{O_2}$	(bar^{-1})	$2.2\cdot10^{16}$	$4.5\cdot10^{10}$
9. $CH_4+2\,O_2 \rightleftharpoons CO_2+2\,H_2O$	−801.1	$p_{CO_2}p^2_{H_2O}/p_{CH_4}p^2_{O_2}$		$9\cdot10^{31}$	$4\cdot10^{26}$
10. $CO+H_2O \rightleftharpoons CO_2+H_2$	− 42.3	$p_{CO_2}p_{H_2}/p_{CO}p_{H_2O}$		1.04	0.33
11. $CO+3\,H_2 \rightleftharpoons CH_4+H_2O$	−206.6	$p_{CH_4}p_{H_2O}/p_{CO}p^3_{H_2}$	(bar^{-2})	$5.92\cdot10^{-3}$	$1.82\cdot10^{-6}$
12. $2\,CO+2\,H_2 \rightleftharpoons CH_4+CO_2$	−248.4	$p_{CH_4}p_{CO_2}/p^2_{CO}p^2_{H_2}$	(bar^{-2})	$6.17\cdot10^{-3}$	$6.05\cdot10^{-7}$

The exothermic reactions 1, 2 and 7 are of particular importance supplying the necessary reaction enthalpy for the actual coal gasification process, the endothermic reaction of carbon and water (reactions 4 and 5), as well as the homogeneous water gas equilibrium according to equation 10, which determines the composition of the gas. The basic principle of all conventional processes for so-called autothermic coal gasification is, therefore, a partial combustion of coal or carbon monoxide which supplies the energy for the actual gasification reaction. This is not the case in allothermic gasification processes using heat from outside the process, for example nuclear heat. In these processes the heat necessary for the endothermic gasification stages does not have to be produced by the partial combustion of the coal. Thus, compared with autothermic coal gasification processes, allothermic processes have the basic advantages of a higher material yield and higher efficiency.

From the reaction equations and equilibrium constants listed in Table 1.1, important conclusions can be drawn as to the composition of the gas and the dependency of the raw gas composition on the reaction parameters, and, in particular, for the special case of the manufacture of synthesis gas for further chemical reactions. Here, synthesis gas is to be understood as mixtures of CO and H_2 containing the smallest amount of impurities possible (inert gases, etc.). For example, the data in Table 1.1 leads to the conclusion that an increase in the reaction temperature favours the formation of CO and H_2, whilst there is a rapid drop in the gasification by-product, methane (Fig. 1.6). There are also fewer hydrocarbons, tars and phenols formed as products of coal carbonization, at the

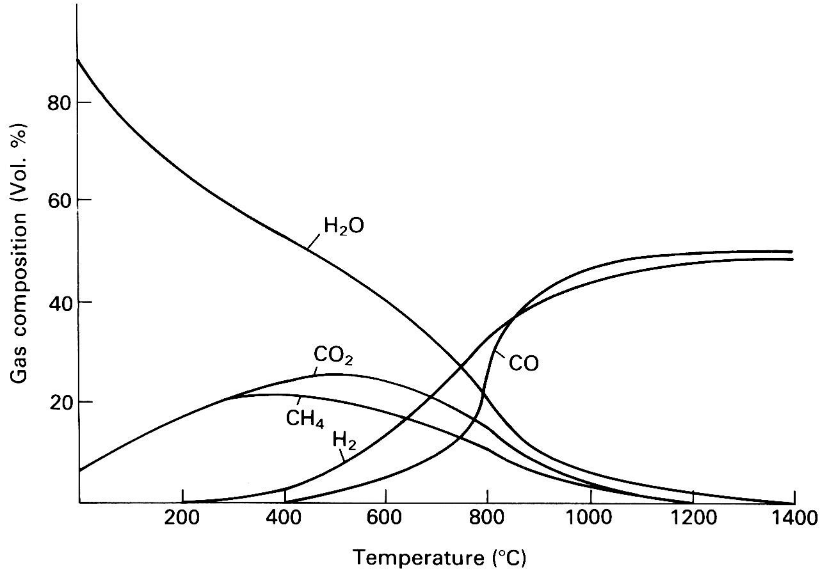

Fig. 1.6. The methane content after $CO+H_2$ formation as a function of the gasification temperature.[9]

higher gasification temperatures. Both effects, namely the highest possible selectivity towards the value product, synthesis gas, i.e. the mixture of CO and H_2, and the purest gas possible, present a strong case for carrying out coal gasification as a high temperature reaction.

However, for various reasons the course of the gasification process cannot be predicted on the basis of thermodynamic data alone. Kinetics play a major role, and are in turn heavily influenced by material and heat transfer phenomena. Figure 1.7 shows the consecutive steps in simplified form, of which, depending on the temperature, one is the slowest and, therefore, rate-determining. The material transport of the gasification agents to the coal grain, and the removal of gasification products from the coal grain, occur simultaneously on the solid, coal, through the diffusion—retarding boundary layer (process (1)), pore diffusion (2) and the chemical reaction of the actual coal gasification process (3).

If the measured, effective rate of gasification is shown as a function of the temperature in the form of an Arrhenius curve, Fig. 1.8 illustrates that gasification below approximately 1000°C is very heavily dependent on temperature because of the temperature dependence of step (3) of the chemical reaction. Above 1000°C, to about 1200°C, the activation energy is halved; at temperatures of about 1200°C the rate of gasification is only slightly dependent on temperature. At the higher gasification temperatures which are required for the reasons of gasification

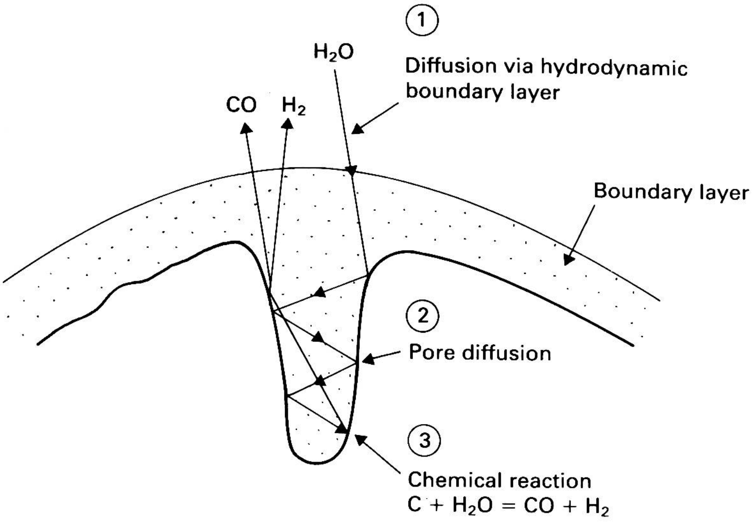

Fig. 1.7. Transport mechanisms of coal gasification.[11]

selectivity already mentioned, the gasification agents, oxygen and water, are already consumed on the surface of a coal grain and the diffusion of the gasification agent through the gaseous boundary layer on the grain becomes the determining factor for the rate of reaction. This has three consequences for the technical control of the gasification reaction:

1 reduction in grain size, i.e. the use of finely grained coal dust, where increase in the specific surface leads to a particularly rapid reaction;

2 a rise in the gasification pressure increases productivity of a given reactor volume;

3 reduction of the diffusion-retarding boundary layer is possible by increasing the relative velocity between gas and coal grain. The technical control of the gasification process should allow for this and permit the required high relative motion of coal and gasification agent by selection of a suitable gasifier.

This suggests the second basic distinguishing characteristic of coal gasification processes—the different engineering solutions found for the selective reaction of the solid coal with gaseous gasification agents. The basic technical processes are:[12–14]

1 gasification in the stationary or slowly moving fixed-bed (fixed-bed gasification);

2 reaction in the fluidized-bed;

3 coal gasification using the entrained-bed principle.

The three processes are characterized by the features compiled in Fig. 1.9.

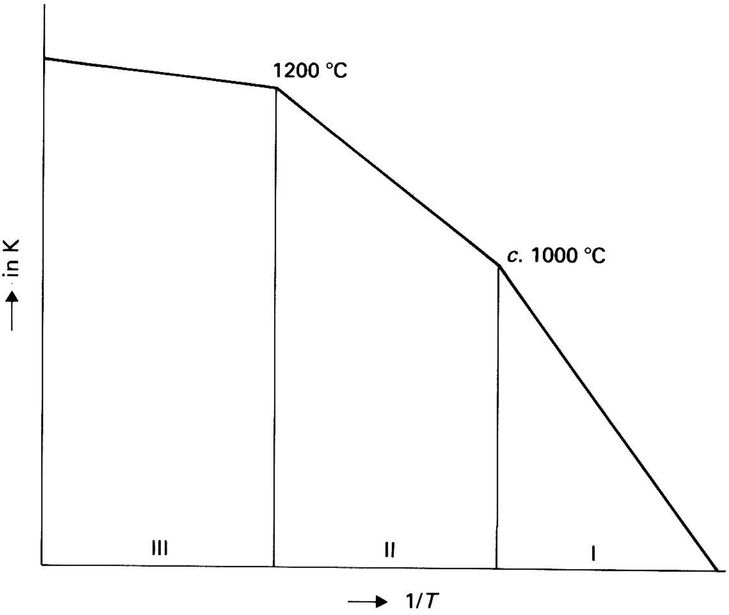

Fig. 1.8. The three characteristic temperature ranges for reaction between gases and porous solids.[10]

Lump coal is normally used in the fixed-bed process where the coal and the oxygen/steam mixture are fed in counter-current at relatively low temperatures resulting in good heat utilization. This reaction control is also favourable from the kinetic point of view since fresh coal encounters largely reacted raw gas. The disadvantages are the coal carbonization caused by the hot gas and the incidence of by-products, such as methane, oil, tars and phenols. Caking coal can only be processed by the use of additional installations such as rotary grates and arms. The technical realization of this process is the Lurgi process.

Finely grained coal (0.5–3 mm in diameter) is used in the fluidized-bed process. The behaviour of the fluidized bed, resembling that of a liquid, permits the continual through-put of coal in contrast to the fixed-bed process, since a constant temperature distribution and a good heat conversion are guaranteed. The disadvantage is the back-mixing of fresh coal with largely reacted coal. In addition, the reaction temperature must be kept below the ash melting point, which, in thermodynamic terms, is a disadvantage, limiting its use so far mainly to brown coal. The Winkler process is the industrial implementation of this process principle.

Entrained-bed processes gasify very finely grained coal in co-current operation. They are independent of the degree of carbonization of the feed material and the caking properties and can also process coal dusts formed during