TECHNO-HISTORICAL ASPECTS OF COAL GASIFICATION IN RELATION TO IGCC PLANTS

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WHAT IS GASIFICATION ?

Gasification can be defined as: "a process in which a solid or a liquid fuel is converted into a combustible gas". The hydrocarbon feedstock is thereby almost always essentially converted by partial oxidation into a mixture of CO and H_2.

Examples of gasification reactions are given below for the oldest of gasification process: coal gasification. For reasons of simplicity coal is represented here as pure carbon and the heat of reaction is given for carbon in the form of graphite.

$C + 1/2\ O_2 = CO$	- 111	MJ/kmole carbon	(A)
$C + H_2O = CO + H_2$	+ 131	MJ/kmole carbon	(B)
$C + 2\ H_2 = CH_4$	- 75	MJ/kmole carbon	(C)

These reactions describe in fact the three ways in which a (hydro)carbonaceous fuel can be gasified, namely by:

exothermic	partial oxidation	(A)
endothermic	reaction with steam	(B)
exothermic	hydro gasification	(C)

In the present report only processes will be discussed in which partial oxidation (A) is the predominant reaction. With dry coal oxygen blown slagging gasifiers the overall reaction is then roughly:

$$2\ CH + O_2 = 2\ CO + H_2$$

where CH stands for the molecular formula of coal and the resulting gas composition is about 2/3 CO , 1/3 H_2.

In relation to reactions (B) and (C) it is observed that Bergbau-Forschung in Germany has worked on a process using indirect nuclear heat for the reaction between coal and steam (B) and Rheinbraun in Germany has worked on a process where brown coal is hydrogasified into methane (SNG) (C).

The first two reactions are commercially also very important using liquid hydrocarbons, LPG and natural gas (methane) as feedstock. In the latter cases where the feedstock is already a gas it is difficult to use the word gasification for the reaction. Therefore instead of gasification the word partial oxidation is used for the conversion of a hydrocarbon gas with oxygen into CO and H_2. For the endothermic reaction of a gaseous hydrocarbon with steam the name "steam reforming" is used.

WHY GASIFICATION ?

Limiting ourselves now to the gasification of coal it is good to ask the question why does such a process exist.
The answer to why gasification has been applied commercially for well over a century is that nature has been benign in that 65-85% of the chemical energy in the dirty solid feedstock is recovered as chemical energy in the clean gas.

Apart from the efficiency consideration given above the answer is that especially for domestic use it is much more convenient to use a (clean) gas than dirty coal. Long before the age of oil and natural gas people had already a preference for a clean combustible product which could be distributed through pipes.

Before 1940 coal gasification comprised the combination of two discontinuous processes namely coke ovens and watergas reactors in which coke was used as a feedstock. The combined process was used to make towngas and the watergas reactors per se were used to make synthesis (syngas) for ammonia, etc. Only after Linde had developed a cryogenic process for the commercial production of oxygen from air did coal gasification become a continuous process in which directly coal could be used for the gasification thus obviating the need for coke for the purpose of making gas.

Basic Processes

In the course of time three basically different continuous oxygen based gasification technologies have been developed:

- Moving bed processes such as the Lurgi dry ash gasifier.
- Fluidized bed processes such as the High Temperature Winkler gasifier.
- Entrained bed processes such as the Texaco and Shell Coal Gasification Process (SCGP)

COAL GASIFICATION MODELLING

The purpose of this modelling is:

- Calculation of the gas composition
- Calculation of the relative amounts of oxygen and steam required per unit coal intake
- Optimization of the cold gas efficiency or syngas yield per unit coal intake
- To provide set points for process control.

Gasifier Calculations

Calculations comprising the gasification proper are based on thermodynamics, mass and heat balances, and process conditions as temperature, pressure and the addition or subtraction of indirect heat.

Gasification makes use of both exothermic and endothermic reactions as was shown above. Generally the desired operating temperature is obtained by judiciously playing with the exothermic and endothermic reactions. The addition of blast (the oxygen containing gas) to the fuel (the feed component containing the carbon) will increase the temperature whereas the addition of moderator (steam, CO_2, inert gas) or the withdrawal of indirect heat or char will decrease the temperature.

Thermodynamics

Gasification is a unique process as in almost all cases it can be very well described by thermodynamics assuming equilibrium conditions. This applies unconditionally to all entrained slagging gasifiers and may also be applied to fluidized bed gasifiers and even moving bed gasifiers provided the latter use coke as feedstock. An exception where it does not apply is for simple moving bed gasifiers where coal is used as a feedstock and the gas moves counter-currently with respect to the coal. In such gasifiers pyrolysis reactions are prevalent in the colder upper part of the reactor and do not allow a simple description of the process by assuming thermodynamic equilibrium. However the thermodynamic approach can always be used in that (hot) part of the gasifier where the actual gasification takes place. An example of the latter is the bottom part of a Lurgi gasifier.

Reactions

In gasifiers where the reactor is essentially filled with coal and/or coke particles the gas composition can be calculated by using the following three independent heterogenic reactions (Ref. 1):

watergas reaction: $C + H_2O = CO + H_2$ + 131 MJ/kmole C (1)

Boudouard reaction: $C + CO_2 = 2\,CO$ + 173 MJ/kmole C (2)

methanation reaction: $C + 2\,H_2 = CH_4$ - 75 MJ/kmole C (3)

As can be seen the reactions involving molecular oxygen are assumed to be complete and do not enter into the calculations.

In entrained gasifiers where relatively little carbon in the form of coal and/or coke is present the gas composition can be calculated by using the following two homogeneous gas reactions:

the CO-shift reaction:

$CO + H_2O = CO_2 + H_2$ - 42 MJ/kmole CO (4)

and the steam methane reforming reaction:

$CH_4 + H_2O = CO + 3\,H_2$ + 206 MJ/kmole CO (5)

Equations

In gasification in its simplest form the following equations will always apply:

- the carbon balance
- the hydrogen balance
- the oxygen balance
- the Dalton equation stating that the sum of
  the mole fractions in the product gas equals "one"
- the heat balance stating that the sum of the
  heat of formation and the sensible heat of the products equals that of the feedstock(s) provided it is corrected for heat which is indirectly added to or subtracted from the process
- the reaction constants of the relevant reactions
  (3 for the heterogeneous case and 2 for the homogeneous case)

Variables

Variables which will always apply are the mole fractions of the gas components:

CO, H_2, CO_2, H_2O, CH_4

The remaining 3 variables may be selected from the following list:

temperature
fuel used per unit (kmole) gas
blast used per kmole gas
moderator used per kmole gas
pressure

Heterogeneous Gasification

Looking now at the number of equations and variables for the case of heterogeneous gasification the following equations are available:

Three equilibrium constants of reactions 1, 2, and 3, four mass and heat balance equations and the Dalton equation.

This leaves the freedom to select 8 variables. The five gas components are fixed and hence there is freedom to select three additional variables from the remaining list of five.

The pressure is dropped from the list for practical reasons as this variable is mostly selected based on how the gas is to be used (e.g. by the required entrance pressure of the gas turbine in case of a combined cycle power station) and the pressure has not much influence on the solutions under the prevailing gasification conditions.

Also the temperature is dropped from the list. When gasifying a known coal mostly the temperature is determined by the softening and melting characteristics of the ash. When the melting temperature is too high ,flux is added to the coal in order to lower the temperature to the desired value.

Whenever we have to work with an unknown temperature it is preferred to work with a trial and error loop where the above proposed simple routine is used rather than with a routine where the temperature becomes a very complicated function of the other variables.

Assuming the temperature and the pressure to be known leaves as the only three variables the ratios of the fuel, the blast and the moderator per kmole of gas. This approach is the same as that followed by Gumz (Ref.1).

Heat of Formation of the Fuel. For the fuel the standard heat of formation may be calculated from the heat of combustion and the elemental composition of the fuel. In case no measured data are available for the heat of combustion this data can be calculated from the elemental analysis. The calculated and the measured data should not deviate more than 2-3% .

Moderator. In most processes the moderator consists of steam. A second possibility is that it stands for indirect heat. This variable may be positive or negative depending on whether the heat is added to the process or withdrawn. It may also stand for the amount of char which is being produced per kmole of gas produced.

Solving the Equations. With the help of the 5 linear equations 5 of the 8 variables may be expressed in the remaining 3 variables which may in turn be solved with the non-linear reaction equilibria constants. After some calculus one 4th degree polynomial in either [CO] or [H_2] will result which can be readily solved and has normally one solution yielding positive fractions for all variables for the gas phase components.
Sometimes a negative solution may be found for the amount of moderator required. In case the moderator constitutes indirect heat removed from the process or char formed in the process such a solution may be perfectly valid. An example of the former process is a fluidized bed gasification process in which the temperature is controlled by a combination of e.g. oxygen addition and steam production in pipes laying in the fluidized bed. Examples where char is produced are the VEW coal gasification process in which air is used as blast and char is produced for later use in a fluidized bed combustor and the second stage of the DOW coal gasification process where char is formed and the blast consists of the hot gas leaving the first stage.

It is also possible that for the most common case of oxygen/steam gasification the steam flow appears to be negative. This situation can e.g. occur in case the coal feed and or the blast contain too much ballast. Examples are:

the use of very low rank coal in SCGP
the use of a coal/water slurry feed as in the Texaco process
the use of air as blast.

In general ballast is water or ash in the fuel or nitrogen in the blast (air gasification).

When this situation occurs the quantity of moderator is set to zero which implies that we have one variable less! The fact that we have landed into the situation where we are able to "produce" moderator in reality means that we have supplied the gasifier with a surplus of gasifying agent (= oxygen + steam). Too much gasifying agent implies that thermodynamically no solid carbon can be present anymore and this in turn implies that we have to apply the homogeneous gasification equations. As there are only two equations in this case there are only two reaction constants and hence the number of variables and equations are again equal.

Homogeneous Gasification

Solving the Equations. By applying a similar procedure as used for the heterogeneous case it is possible to express all variables in terms of [CO] and [H_2] using the linear equations. Further the reaction equilibria constants yield 2 non-linear equations. Rearrangement and elimination yields an 8th degree polynomial in either [CO] or [H_2].

A complication is that sometimes two apparently valid solutions are found: one with "normal" gas concentrations and one in which the concentrations of [CO_2] and [H_2O] are very low and where that of [CH_4] is relatively high. Filling in these concentrations in one of the equations (1), (2) or (3) teaches that solid carbon can thermodynamically be formed! This is a nice illustration of the fact that although the equations (1), (2) and (3) always imply equations (4) and (5) the opposite is not true. Three equations contain more information than two equations!

When the first heterogeneous approach does not yield a valid solution the second homogeneous one normally will give a solution. However, when a solution is required at e.g. a temperature of 4000°C also the homogeneous approach will not give a solution as there is no way that such temperatures can be reached even when going to complete combustion with oxygen.

Entrained Gasification. A unique property of entrained gasification is that it is the only type of gasifier which enables the user to work with an overdose of gasifying agents (oxygen and steam) at all times.

This in contrast to moving bed- and fluidized bed gasifiers where always solid carbon is present.
In fact almost all entrained gasifiers (an exception is the VEW process) operate with a slight surplus of gasifying agent in order to limit the slip of unconverted carbon. Although thermodynamically carbon cannot exist in this case some of it can always pass the reactor because of insufficient residence time and/or because it was "hidden" in flyslag.
Too much gasifying agent is expensive (oxygen) but too little will e.g. increase the carbon content of the flyslag which is often recycled to the coal feed and subsequently to the gasifier. This constitutes a penalty as this material has to be heated again to gasifying conditions. Careful optimization of all variables is always required.

The option of working with an overdose of gasifying agent in a region where the homogeneous reactions govern the process leads to unique optimization possibilities as described below.

Real Coal

The above calculations were based on a solid oxygen containing hydrocarbon. In practice coal will contain hetero atoms as sulphur and nitrogen and further ash. Moreover the oxygen used as blast will always contain some argon. These complications imply that the element equations have to be extended with a sulphur, a nitrogen and an argon equation and further we need an ash equation. The four equations are required to solve the following variables: H_2S, N_2, A and ash/slag respectively. As all these equations are linear they hardly complicate the calculation procedure. The procedure can be further refined by assuming that a certain percentage of the sulphur is converted into COS and of the nitrogen into HCN and NH_3.

THE COAL FINGERPRINT

For a good understanding of the partial oxidation of any particular feedstock whether coal, liquid or gas it is very useful to calculate a gasification fingerprint.

Instead of the more correct general terms: partial oxidation, fuel, blast and moderator the more restrictive: gasification, coal, oxygen and steam will be used respectively.

A most instructive representation comprises a graph were for a chosen heat loss and a specific set of reactants coal, oxygen, and steam, each with a fixed temperature and composition, the steam consumption per unit coal is plotted along the axis and the oxygen consumption per unit coal along the abscissa (see Figure 1).

The straight line (A-A) on the left of Figure 1 represents the minimum amount of gasifying agents (oxygen and steam) which are required to gasify the coal assuming no CO_2, H_2O and CH_4 are formed. Thermodynamically this is not possible and hence the real thermodynamic equilibrium situation is represented by the thick solid line, which gives the minimum amounts of oxygen and steam required for each temperature. This line is calculated with the heterogeneous gasification equations. It very well describes processes where the reactor is essentially filled with coal as e.g. in the lower part of moving bed gasifiers and in fluidized bed gasifiers. In case we want to do the calculation for temperatures above that corresponding to the intersection of the thick line with the abscissa, we have to set the moderator flow to zero and look for a "homogeneous" solution. By doing this the solutions for the various temperatures are found along the abscissa at the right of the intersection of A. By gasifying with fixed oxygen/steam compositions above the thermodynamic minimum amount required to avoid solid carbon, the isotherms drawn in Figure 1 can be generated. We can repeat this procedure for various heat losses which will give the complete finger print .
However, we should not forget that in these plots some secondary variables have to be set constant. An example is the carbon conversion.

PROCESS CONTROL

Gasification Temperature

In relation to process control it is observed that gasification temperatures are virtually impossible to measure. Thermocouples succumb to the harsh conditions and radiation methods have the problem that it cannot be established whether the radiation of the solids or from the gas is measured. The complication is caused by the fact that the particles which still contain carbon exhibit a "chemical wet bulb temperature". This phenomena is explained by Van Loon (Ref.2) which proved that the solid carbon reacts only via endothermic reactions with CO_2 and H_2O. The reaction products CO and H_2 react partly with oxygen in a sort of halo surrounding the coal particle. The result is that the carbon containing particles have always a lower temperature than the surrounding gas (see Figure 2).

Process Indicators

When trying to optimize the operating conditions for a certain coal it is always good first to carry out the calculations for the heterogeneous case as this will inform the operator about the minimum ratios of oxygen and steam required. A small departure from this minimum by e.g. making the calculations for a minimum concentration of CO_2 in the gas of 1 - 1.5% vol. can then be used to obtain the real operating values (this for SCGP). Moreover such a departure from the minimum is required to create room for process control.

It is very instructive to draw the iso- CO_2 and iso- CH_4 lines in the graphs (see Figure 3). The fact that the iso-CO_2 lines run more or less perpendicular to the isotherms and the iso-CH_4 lines more or less parallel imply that the CH_4 content of the product gas is a better indicator of the temperature in the gasifier than the CO_2 content. The latter can be used only in case a the ratio of oxygen to steam is fixed and in the region where only oxygen and no steam is required for gasification.

Using both CH_4 and CO_2 possibly in combination with the heat loss which can always be readily measured from the reactor wall steam make in case of a tube wall gasifier is generally sufficient to monitor gasifier performance.

The Gasifier Outlet Temperature as a Function of the Gas Analysis

To calculate the gasifier (outlet) temperature from the gas analysis is not a simple affair. The reason is that it is (as yet) not possible to analyse the gas directly after it leaves the gasifier. Sometimes it is suggested that this can be done by drawing a small sample through a thin almost capillary pipe and then analysing the composition. The idea is that by doing this the equilibrium will be frozen in quickly and the composition measured upon analysis will be the same as at the gasifier outlet. It should be realized though that the thin tube required for fast cooling is generally made of high alloy steel containing nickel or another catalytic component and that it implies that the gas sample is exposed to a relatively large surface area of material which could catalyse both the shift and methanation reactions and thus rendering the analysis worthless.

Working with the Gas Analysis

In general the gas is best analysed downstream of the quench/syngas cooler. Also in this case the analysis has to be corrected because of the change in composition caused by the fact that the e.g. the CO-shift reaction freezes in at temperatures below that prevailing in the gasifier.
Cooling the gas by quenching (e.g. with water) and indirect cooling makes that down to a certain temperature the CO-shift reaction will adjust itself and from that temperature downwards we will have a purely physical quench and cooling (see below). The temperature of freezing in can be calculated from the gas composition by the following procedure:

Upon passage through the quench the gas will cool down from Tin to Tout as shown in Figure 4. When the composition of the gas leaving the syngas cooler is analysed a chemical equilibrium constant Keq can be calculated for the reaction in question (in the example the CO-shift reaction) and the temperature Teq(1) to which this equilibrium corresponds is also plotted in the graph. It can be readily seen that this temperature is generally much higher than the temperature at which the gas leaves the quench/syngas cooler. The procedure which is now followed is that the composition of the gas is re-calculated for the case where say 10% less quench medium was used. This is perfectly realistic as this last 10% only led to pure "physical" cooling. The gas leaving this "shortened" quench has a higher temperature than the previous Tout and with the newly calculated gas composition (this only in case a quench is being used) it is possible to calculate a new Teq(2) which is lower than Teq(1). This procedure can be repeated and at a certain location the two curves which are developing will intersect. The temperature at which this occurs is the temperature at which the equilibrium froze.

The data represented in Figures 1, 3, 5 and 6 have been obtained taking into account the effect of the adjustment of the CO-shift reaction. It is seen that when the temperature of freezing in the equilibria have been assumed to be equal that the composition of the gas leaving the syngas cooler still clearly reflects the differences in temperature in the reactor.

Optimum Operating Point

IGCC Application. The fact that gas can be much more efficiently converted into electricity in a combined cycle (well over 50%) than coal per se via a steam cycle (about 40%) is the main reason why the efficiency of an IGCC is higher than that of a conventional coal fired power plant. Moreover even if the conventional power station is equipped with scrubbing facilities it is less environmentally friendly than an IGCC.

The optimum operating condition for a gasifier depends both on the type of feedstock and on the application.
For fuel gas applications like in combined cycle power stations the gasification should be carried out at as low a temperature as possible as this will results in the highest cold gas efficiency (see Figure 5 where iso-cold-gas-efficiency lines have been drawn). Although fluxing may help to create a larger operating window for coal the minimum temperature will always be limited by the ash melting characteristics and/or the coal reactivity. Temperatures below 1400 for low rank coal and below 1500 for hard coal will not be practical for slagging gasifiers.
Operation as close as possible to the thermodynamic equilibrium line (see Figure 1) is indicated. In other words operation with the minimum amount of gasifying agent.

The above procedures can help the operator to optimize the cold gas efficiency. This is a very important efficiency indicator for an CGCC but should never be used to compare CGCC schemes using different gasifiers. In that case only the total CGCC efficiency should be used for comparison.

Synthesis Gas Application. For synthesis gas applications the situation is different. In this case the amount of moles per unit feedstock has to be maximized. The effect of the operating conditions on this maximum is illustrated in Figure 7. The optimum along the abscissa is caused by the fact that at lower temperatures more $CH4$, CO_2 and H_2O are present. There is also a maximum along the ordinate. This is caused by the CO-shift reaction which is exothermic and not indicated in Figure 6.

The latter effect is slight but it is there. The result is that for a fixed heat loss and reactant composition there is generally one point which yields the maximum amount of synthesis gas. In fact the above effect for optimizing the production of syngas is probably only relevant in the case of oil gasification as the ash limitations in coal gasification do not allow the operation at sufficiently low temperatures where this effect becomes relevant.

MISCELLANEOUS

Air Gasification

Often the question is raised why air is not used as blast in IGCC. The expensive oxygen plant can then be saved and for the application of combined cycle power generation a high gas purity is irrelevant. It is even so that the nitrogen which is coming available from the oxygen plant is later added to the treated gas before it is being combusted in order to diminish the NOx formation in the gas turbine.

The fact is that going for air gasification results in an about 20% lower cold gas efficiency of the gas and a correspondingly higher duty of the - expensive - syngas cooler.
Hence the contribution of the electricity production via the steam cycle which has an efficiency of about 40% increases at the cost of the contribution via the more efficient (50%) combined cycle. This loss is for modern gas turbine ICGCC plants higher than the additional power required for the compressors in the oxygen plant.

Coal Reactivity

Of course the gasification performance of different coals varies depending on their intrinsic reactivity. Scale up rules for gasification reactors are generally such that the residence time increases with increased reactor size. For this reason coal reactivity is not a very important parameter.

In case one nevertheless would like to incorporate intrinsic activity in a design or for interpretation of plant results a graph of the oxygen content of the maf coal versus the carbon conversion is a very practical and simple tool. Often such a graph has to be made based on plant results and can then later be used for forecasting the performance of future coals based on their ultimate analysis.

CONCLUSIONS

- Based on the analysis of the feedstock components a coal fingerprint can be calculated which indicates for each high temperature gasification process the optimum operating point.
- In the analysis of the above calculations it should be taken into account that the thermodynamic equilibrium of e.g. the CO-shift freezes in at a temperature which is lower than the outlet temperature of the gasifier.
- The best process indicators are the CO2 and CH4 content of the gas. Another important indicator is the steam make from the gasifier wall in case a tube wall gasifier is used.
- It is emphasized that the procedures discussed can only be used to optimize the cold gas efficiency of a certain type of gasifier. To compare CGCC's using different types of gasifiers the efficiency of the total ICGCCs should be optimized.

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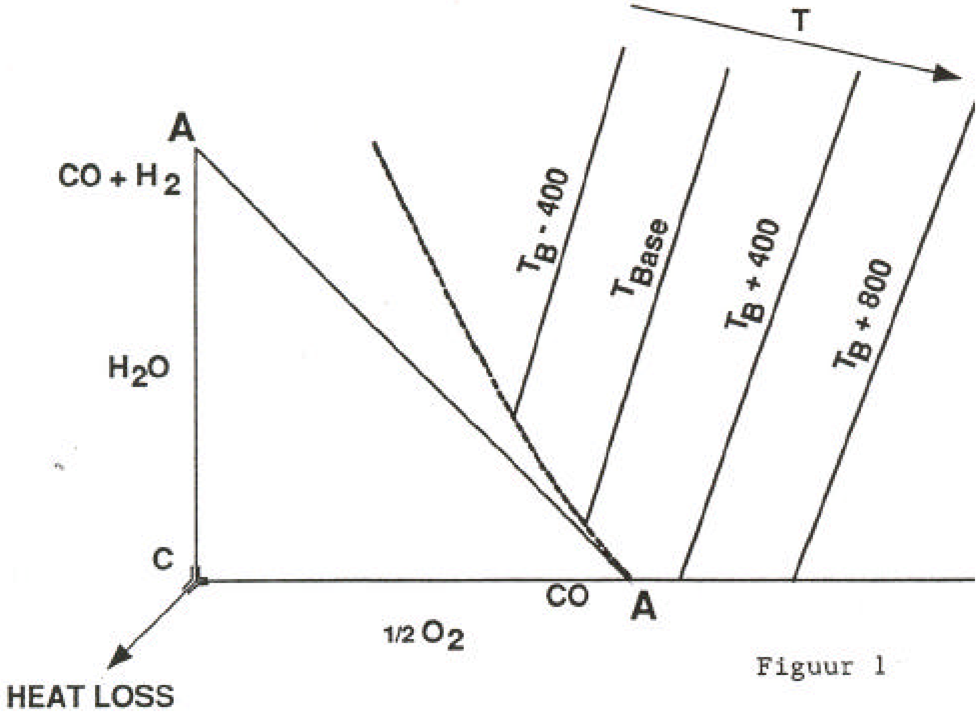
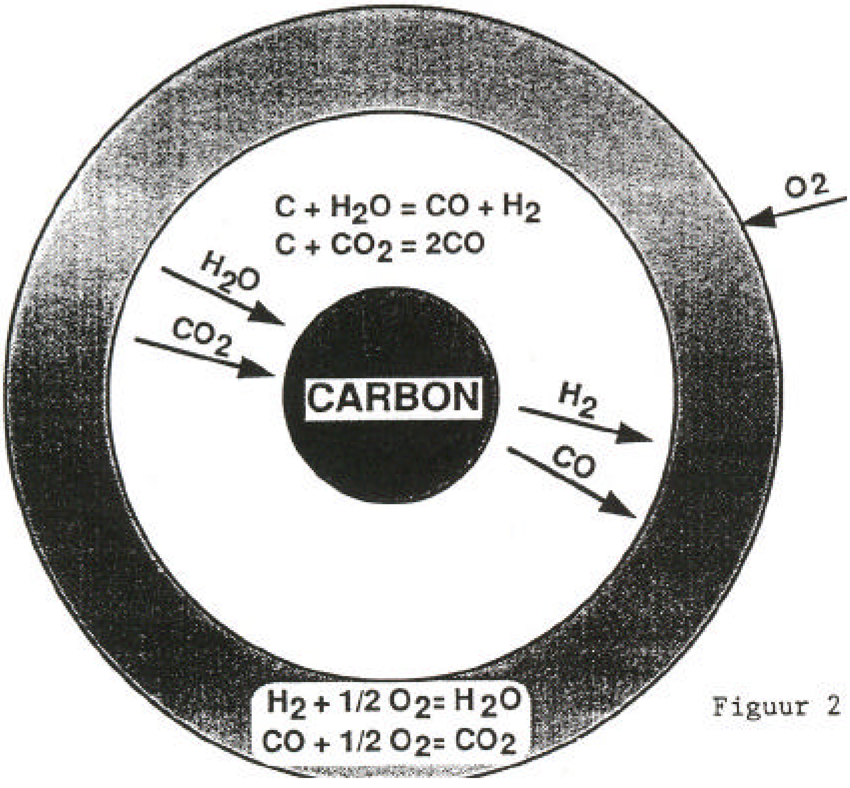
GASIFICATION

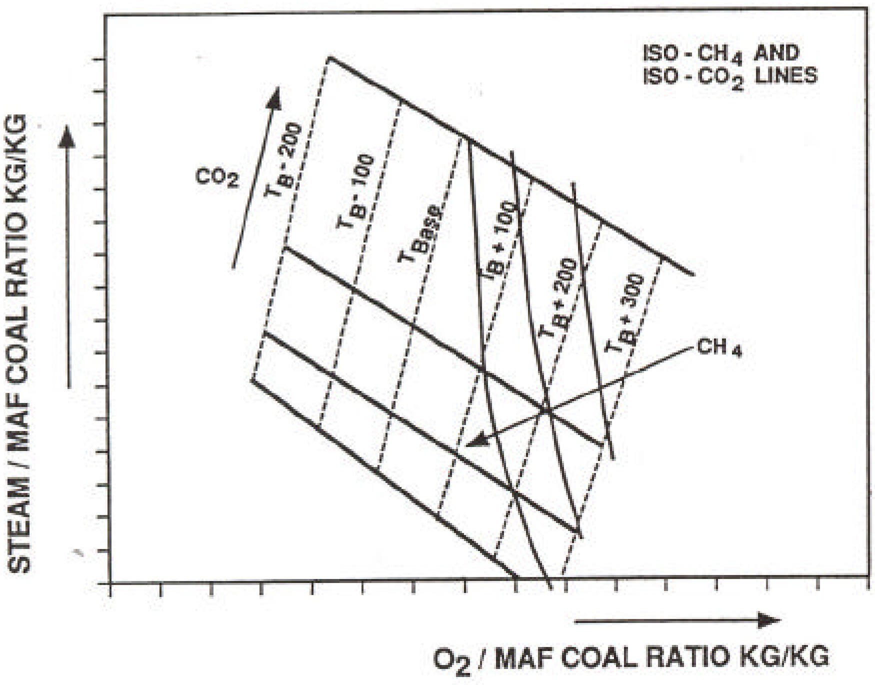


Figuur 1

GASIFICATION MECHANISM



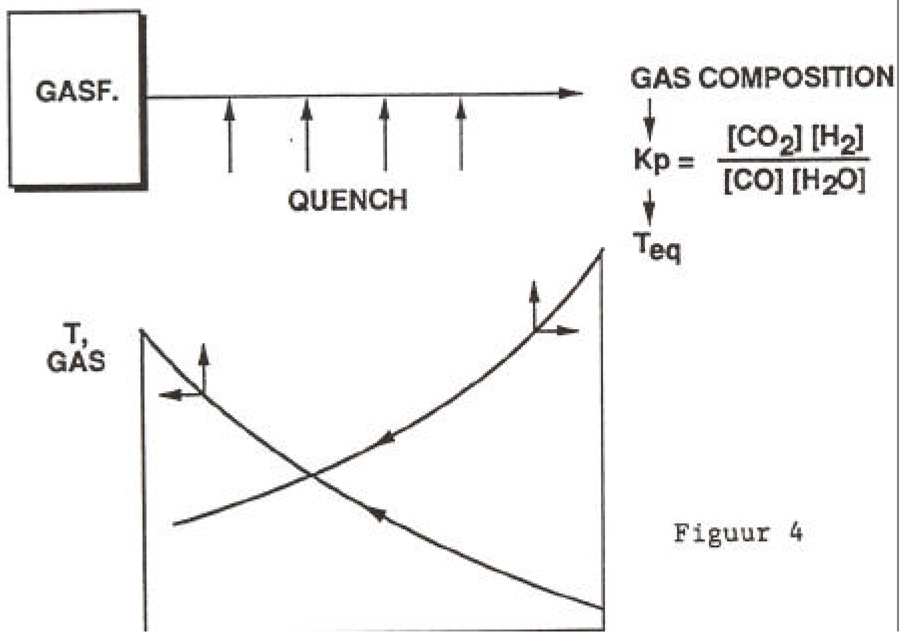
Figuur 2



Figuur 3

CALCULATION OF EQUILIBRIUM TEMP. OF SHIFT REACTION

$CO + H_2O = CO_2 + H_2$



Figuur 4