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Abstract
One of the CHRISGAS project objectives is to study the shift catalysts in biomass-generated synthesis gas. The water gas shift reaction is ruled by equilibrium, and the state of the gas can for a given H_2/CO ratio be shifted by addition/removal of water, CO_2 and/or by a change in the temperature. Stability area in respect to gas composition, sulphur content, pressure and temperature for FeCr shift catalyst has been investigated by thermodynamic equilibrium calculations. The calculations show that carbide formation is favourable in the ''Normal water'' case without sulphur in the gas. If sulphur is present in the gas, the situation improves due to sulphide formation.

KEY WORDS: water-gas shift; iron-chromium catalyst; carbide formation; sulphide formation.

1. Introduction

In the search for a sustainable transport fuel, one possibility is synthetic fuels generated from biomass. In order to use processes such as Fischer-Tropsch, methanol, DME and the Mobile process, one needs to produce synthesis gas from the biomass first. The key steps are gasification, reforming/partial oxidation and the shift process. In the gasification step, if oxygen is used as an oxidant, the solid biomass is converted into a solid residual (ash) and a gas consisting mainly of CO, CO_2, H_2, H_2O, lower hydrocarbons (CH_4 and C2) and some tars. The hydrocarbons and the tar will be converted into CO, CO_2 and hydrogen in the reformer/partial oxidation step. When the gas leaves the reformer/partial oxidation step the H_2/CO ratio will be close to 1 [1]. To utilize the synthesis gas in the subsequent synthesis steps, the H_2/CO ratio has to be tuned to the optimum value for the process in question. This is done in the shift step. The water gas shift reaction (1)

$$CO + H_2O \longleftrightarrow H_2 + CO_2 \qquad (1)$$
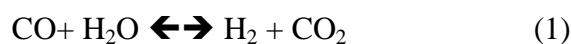
is ruled by an equilibrium, and the state of the gas can, for a given H_2/CO ratio be shifted by addition/removal of water, CO_2 and/or by a change in the temperature. In this study the stability area in respect to gas composition, sulphur content, pressure and temperature for FeCr shift catalyst will be investigated by thermodynamic equilibrium calculations.

2. CHRISGAS project and Värnamo pilot plant

The CHRISGAS project is sponsored by the EU and the Swedish Energy Agency (STEM) and has as an objective to demonstrate large-scale production (3500 Nm3/h) of synthesis gas from biomass by 2009. The project consists of two parts; CHRISGAS concerning R&D work on various parts of the process and a second part concerning the rebuilding of the IGCC plant located at the Växjö -Värnamo Biomass Gasification Centre in Sweden [2]. According to the time schedule the plant should be ready for the first test runs in 2009. After rebuilding, the plant (figure 1) will have been changed from air to oxygen-steam-blown. A hot gas filter will purify the gas from dust. Oxygen and steam will be added to the gas before the reformer unit where residual hydrocarbons and tar are converted. The H_2/CO -ratio will be shifted in a HT shift reactor. If the gas requires shifting to low H_2/CO value (for instance H_2-production) the unit will also contain a LT shift reactor. The plant will be equipped with an autothermal

reformer/partial oxidation (ATR/POX) step and a shift step. In the present planning, the shift step is equipped with a bypass with variable flow. By varying
the ratio between the shifted and the un-shifted flow, a synthesis gas with desired composition can be obtained.

3. Unit operations in the plant

Several major unit operations will be performed within the plant to produce the hydrogen rich synthesis gas. The solid biomass must be gasified, the gas cleaned from solid particles, remaining hydrocarbons converted and finally the H_2/CO ratio should be tuned to fit the subsequent synthesis step. The gas purification steps, sulphur removal etc. are, at the present, not included in the project. In table 1, the estimated gas composition after the
gasifier is given (5). Those values were estimated, within the consortium, from the expected change in gas composition when switching from air blown to oxygen
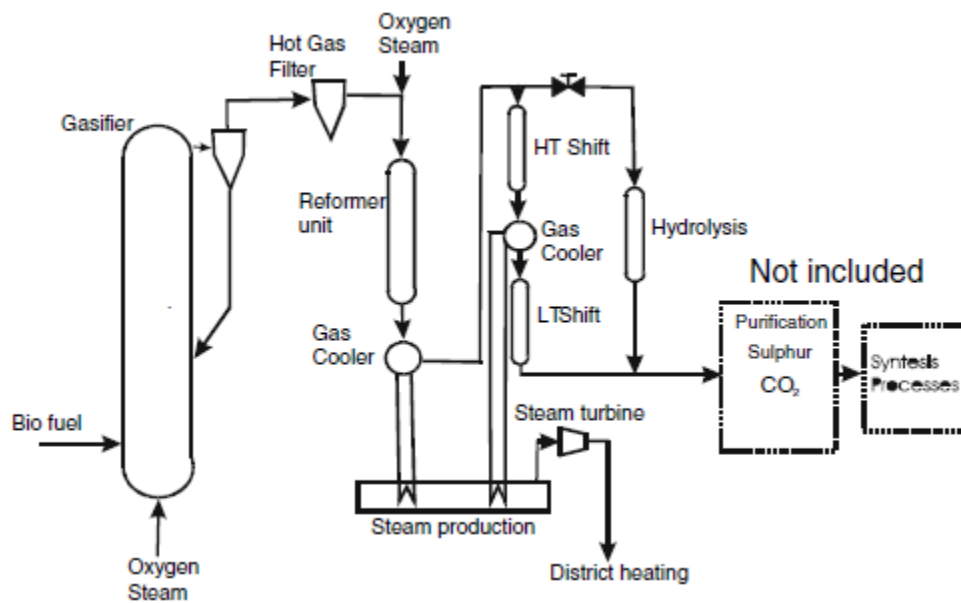

Figure 1. The Värnamo plant after rebuilding

blown gasification. When better data are available, those values will probably be adjusted. However, the given gas composition have been used as a base for the further calculation presented in this paper. For the heat and equilibrium calculations HSC 5 from Outokompu have been used.

3.1. The gasifier

In the gasifier the solid biomass is converted into gaseous components and ash by partial combustion. If oxygen is used instead of air, the dilution of the synthesis gas with nitrogen is avoided and the heat value of the produced gas increases. A multitude of chemical processes take place in the biomass due to the released heat and released or added steam. The produced gas consists mainly of carbon monoxide, carbon dioxide, hydrogen and water vapor (table 1). There will also be a fraction of low hydrocarbons, like methane CH_4 and C2 to C3 hydrocarbons. More or lesser amounts of tars are also present. Tars consist of polyaromatic hydrocarbons with high boiling point, the lightest molecule considered, as tar is naphthalene (white tar). As minor components ammonia and sulphur compounds, mainly H_2S, is present in the gas products. The exact composition of the gas after the gasifier depends on several factors, like type of gasifier, conditions in the gasifier and type of fuel. The Värnamo gasifier

3

is a 18 MW$_{th}$ circulating fluidized bed gasifier, pressurized to 10–15 bar. In table 1, the estimated gas composition after the Värnamo gasifier is given. The low heating value (LHV) is calculated as the heat of combustion of the given gas mixture at 25 °C, using naphthalene as the tar component.
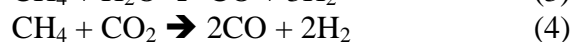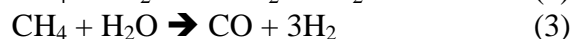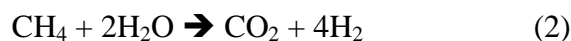
Table 1
Estimated composition of the synthesis gas in Värnamo (Thermodynamic calculations)

Component	After gasifier (vol%)	After ATR 1000 °C (vol%)	After POX 1300 °C (vol%)
Inlet O$_2$		7	10
Inlet Temperature C		800	800
C2-hydrocarbons	1.6		–
CH$_4$	8.2	–	–
CO	11.9	23.8	24.3
CO$_2$	27.9	19.8	19.2
H$_2$	11.8	23.0	16.1
H$_2$O	37.7	33.4	39.7
NH$_3$	0.3	0.2	0.2
H$_2$S	0.01	0.01	0.01
Tars	0.3	–	–
Massflow ratio kg/kg[a]	1	1.13	1.19
Supplied heat MJ/kg[b]	–	0.25	0.37
LHV MJ/Nm[c]	7.3	5.4	4.8
LHV MJ/kg	6.6	5.6	4.8
LHV×MFR[c] MJ/kg	6.6	6.3	5.7
Efficiency[d]	–	0.92	0.80

[a] Gasifier outlet; [b] By the injection stream (H$_2$O(l) + O$_2$(g) (25 °C) → H$_2$O(g) + O$_2$(g)(800 °C) MJ/(kg gas after gasifier)); [c] MFR = Mass-flow ratio; [d] (LHV$_{out}$ x MFR$_t$-supplied heat)/LHV$_{in}$ x MFR

3.1.1. The reformer

When the gas leaves the gasifier, it contains lower hydrocarbons (methane, ethane, ethene, etc.) and some tars (table 1). The lower hydrocarbons represent approximately 50% of the heat content in the calculated LHV-value while the tar stands for approximately 10% of the heat content. If the purpose of the plant is to produce synthesis gas suitable for liquid synthetic fuel production in an economic way, the lighter hydrocarbons and the tars have to be converted into synthesis gas as well. This is done in the reformer step by reacting the hydrocarbons with water vapour and carbon dioxide, for instance methane:

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \qquad (2)$$
$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (3)$$
$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad (4)$$

All of the reactions are endothermic and heat has to be supplied to reaction vessel or the temperature will drop and the reactions will stop. Methane is the most stable hydrocarbon in the reforming reaction because it is difficult to activate and there exist equilibrium between methane and the synthesis gas. In figure 2 the calculated (HSC 5) equilibrium methane conversion, at 1 bar, versus the temperature is shown at two different molar steam/carbon ratios, 1 and 3. As can be seen in the figure 2, the lower temperature, the more water is required to obtain full conversion of the methane. The classical reforming process is the steam reforming, using a nickel-based catalyst, were the required heat for the reaction is supplied externally. This means that heat have to be transferred from the outside, through the reactor walls (multiples tube package) into the reactor. To avoid material issues, the temperature have to be as low as possible (maximum 850 °C). This makes it necessary to use steam/carbon ratios of about 3. It is still difficult to obtain full conversion of methane in a steam reforming process and therefore it is often supplemented by a secondary reformer unit. The secondary reformer unit can also be used as standalone reformer unit, autothermal reformer (ATR) (figure 3). In such unit the required heat is generated directly in the reactor by adding air or oxygen to the fuel and partly burns it. The reactor is lined with one or several layers of

refractory oxides to protect the metal casing from the high temperature in the reaction zone. This makes it possible to run the reactor at higher temperature (900–1100 $^{\circ}$C) compared with steam reforming.
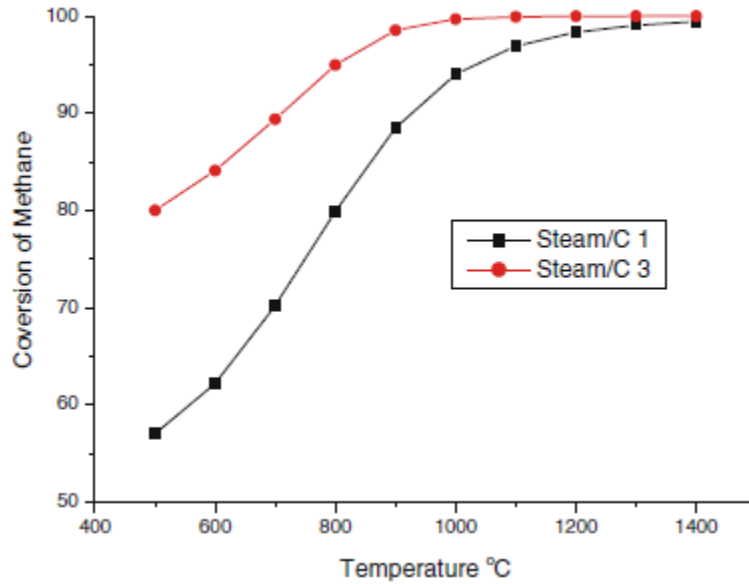

Figure 2. Reforming of methane. Calculated equilibrium methane conversion at steam/carbon ratio 1 and 3.
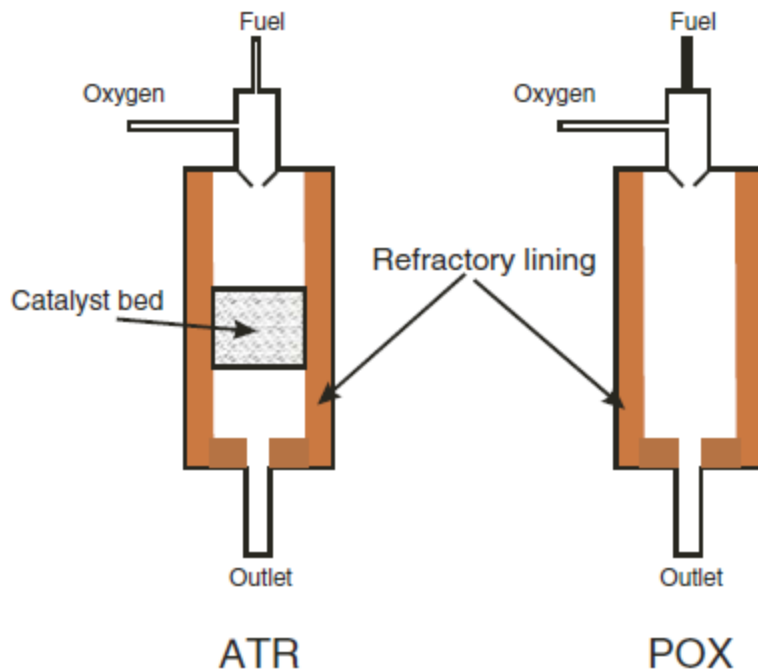

Figure 3. Principle construction of an ATR and POX unit.

ATR units also use nickel based catalysts, but with lower nickel contents to improve the temperature stability of the catalyst. It is also possible to perform the reforming with air or

oxygen addition homogenously in the gas phase, partial oxidation (POX), without solid catalyst in a unit very similar to the ATR unit (figure 3). Due to the lack of catalyst POX requires yet higher temperature than ATR to work, 1200–1400 ^{o}C. In table 1 the outcome by using ATR and POX has been calculated by the use of HSC 5. Incoming gas by the composition given after the gasifier has been used assuming 15 bars pressure and 800 ^{o}C in the inlet gas stream. It is assumed that the equilibrium is reached in the reactor and there are no heat losses. The added oxygen is provided as an equimolar O_2/steam stream at 800 ^{o}C. The C2-hydrocarbon is assumed to be ethylene and the tars naphthalene, the ammonia and hydrogen sulphide are not participating in the calculation. The calculation was performed iteratively, for given oxygen/steam addition the gas phase composition was calculated as function of temperature, and then a temperature was assumed. The gas phase composition corresponding to the assumed temperature was then put into the heat balance calculation and the outgoing temperature was solved. This was repeated until the assumed and the calculated temperature differed less than 10 ^{o}C. Because of the injection of the O_2/H_2O mixture, the mass flow will increase (table 1). Due to the mass flow increase the LHV of the gas leaving the gasifier is not comparable with the LHV calculated after ATR and POX on weight or volume basis. By multiplying the calculated LHV (weight based) with the mass flow ratio between the gas before and after the O_2/H_2O injection, a comparable value is obtained. Since the O_2/H_2O stream is injected as 800 ^{o}C hot gas instead of oxygen and liquid water at 25 ^{o}C, it also represents a stream of supplied heat (table 1). The efficiency value in table 1 shows the fraction of chemically bounded heat in the gas still remaining after the unit operation.

3.1.2. The shift
When the gas leaves the reformer unit, the ratio between H_2 and CO is close to 1 (table 1). To use the produced gas in subsequent synthesis processes, for instance Fischer-Tropsch, the ratio should be close to 2. The role of the shift steps [3,4] is to tune the ratio between H_2 and CO to the desired value according to the water gas shift reaction [5]. This reaction is ruled by equilibrium (figure 4). The equilibrium position can be changed by a change in temperature and/or a change in the concentrations of one or more of the components, for instance by addition of water. However, to convert the majority of the CO into CO_2 (for maximum hydrogen production) low temperature is required. Traditionally this process is performed in one High Temperature (HT) step and one subsequent Low Temperature (LT) step with a cooling step in between (figure 3). The reaction is only mildly exothermic and is usually carried out in adiabatic reactors.
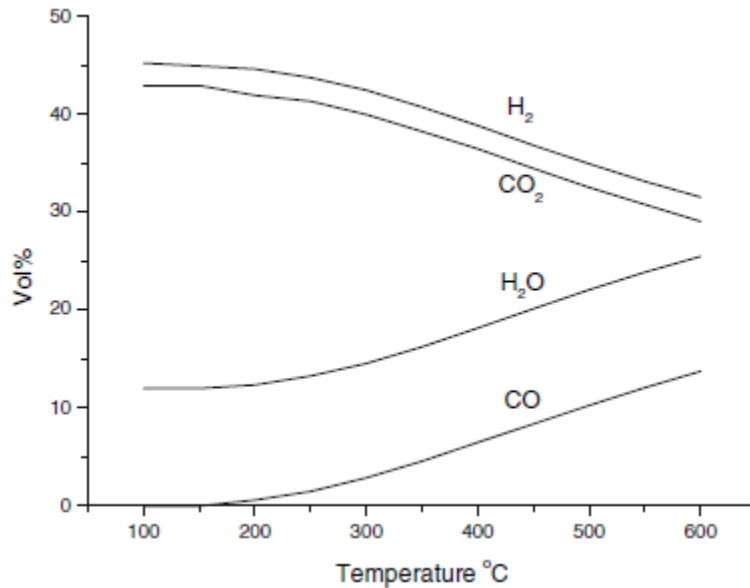
Figure 4. Calculated WGS equilibrium composition as function of temperature. Inlet gas composition given in table 1 (after ATR)

3.2. High temperature shift step

The high temperature shift step using FeCr catalyst was introduced by BASF in 1915. It's essentially the same process and catalyst used today [3,4]. The catalyst consists of magnetite Fe_3O_4 in its activated form and Cr_2O_3 that acts as a promoter, stabilizing the magnetite crystals. The catalyst is resistant towards sulfur in that sense that the iron is converted into FeS. The FeS also acts as a shift catalyst but with reduced activity, and using more catalyst can compensate for this decrease.

3.2.1. Low temperature shift step, Cu/ZnO catalyst

The classical low temperature shift catalyst is the Cu/ZnO [3,4]. It exhibits high activity in the shift reaction at approximately 200 °C. The use of the catalyst is limited downwards in temperature by the dew point of the gas and upwards in temperature by sintering of the copper, above 260 °C. The catalyst requires almost sulphur free environment since both the Cu and the ZnO forms inactive sulphides.

3.2.2. Low temperature shift step, CoMo catalyst

When Cu/ZnO cannot be used because of high sulphur content, the sulphur resistant CoMo catalyst can be chosen [3,4]. This catalyst actually requires sulphur in the feed because it is active in the sulphidized form. The catalyst can also be used as a HT shift catalyst, but the higher the temperature, the higher the sulphur content is required in the gas to keep the catalyst in the sulphidized state. The low temperature limit is set by the dew point of the gas.

3.3. Hydrolysis step

Organic sulphur in the fuel will be converted into, predominately, hydrogen sulphide (H_2S) in the gasifier. This sulphur needs to be removed prior to the fuel synthesis steps, this is done by an absorption step, for instance by ZnO or by scrubbing in an amine solution. However, a part of the sulphur will be in the form of carbonyl sulphide COS. In this form the sulphur will not be removed by the absorption step.
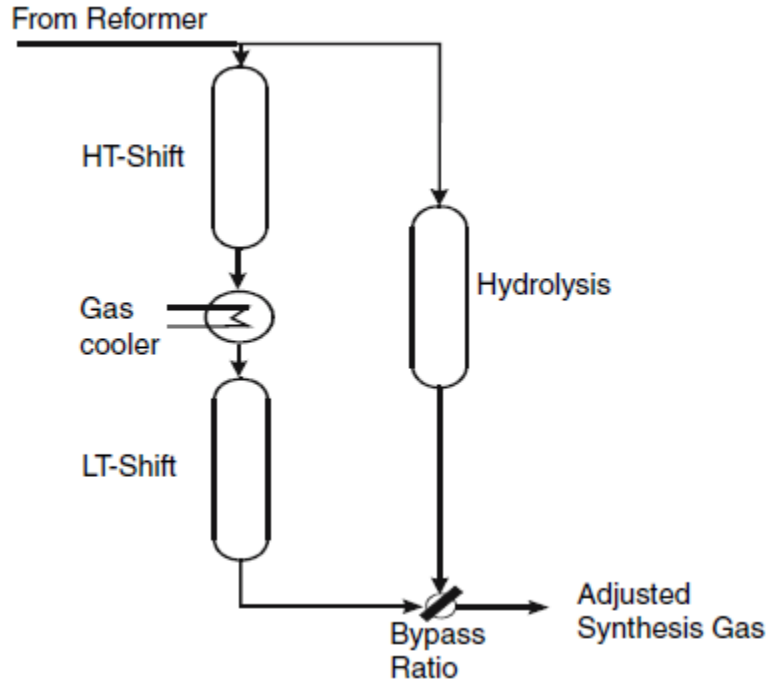
Figure 5. Planned shift steps in the Värnamo plant. Normally the COS is converted by the FeCr catalyst into H_2S by a hydrolysis reaction (5) [3]:

$$COS + H_2O \longleftrightarrow CO_2 + H_2S \qquad (5)$$

In the Värnamo plant the H_2/CO-ratio should be tuneable. This could be done by controlling the reactor temperatures and for instance by controlled water addition. However, operating the shift step in a flexible mode is more complex and slower than operating it in a constant mode. Therefore, the H2/CO-ration tuning is planned to be performed by a controlled bypass flow (figure 5). This means that the bypass flow will not be treated by the FeCr catalyst and the total gas flow after mixing with the shifted gas will contain COS. Therefore it is necessary to add a hydrolysis step to the bypass flow. The catalyst for this reaction is activated alumina and the reactor should be kept 40–50 ^{o}C above the dew point.

4. Research activity

Except for the main components, the produced synthesis gas also contains minor components like hydrogen sulphide, dust, aerosols and volatile metals that might decrease or destroy the performance of a catalyst. Although the problems are expected to be much less in the shift step than in the reformer step there are some matters that will have to be investigated. In the first part of 2006 a micro reactor system will be taken into operation at Växjö University to enable studies of the shift reaction up to 20 bars, using FeCr catalyst.

4.1. Stability of catalysts

The bio-mass generated synthesis gas contains up to 100–150 ppm of sulphur compounds, i.e. H2S. If the sulphur is not removed prior the shift step, the catalyst must be sulphur resistant [2]. This rule out, for instance, copper based catalysts. Sulphide based shift catalyst, on the other hand, requires a sufficient amount of sulphur in the feed to stay active.

4.2. Calculations and discussion

The normal active phase of FeCr shift catalyst is magnetite Fe_3O_4. The Cr is in the form of chrome (III) oxide, Cr_2O_3, and acts as a textural promoter by stabilizing the magnetite crystallites [4]. However, the composition of the solid catalyst depends on the composition of the gas phase, the temperature and the pressure. In figure 6A–F thermodynamic calculations (HSC 5) are presented of equilibrium compositions of the Fe phase in the catalyst as a function of the gas composition. Thermodynamic calculations are very useful but the outcome depends on the quality of the data used and if all relevant compounds are present. As an initial value 1 kmol of Fe(s) was chosen as the solid phase in contact with a gas phase consisting of totally 1E6 kmol and the composition given in table 1 after ATR. In the solid phase, the following Fe-species were included in the calculation:

$FeCO_3$, $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, FeO, $FeO_{1.5}$, Fe_2O_3, Fe_3O_4, $FeSO_4$, $Fe_2(SO4)_3$, FeS, FeS_2, Fe_2S_3, Fe_7S_8, Fe_3C, Fe_5C_3, Fe.

Figure 6A show the catalyst compositions in the presence of a H_2/H_2O ratio of 0.7 that will be denoted in the calculations as the ''Normal water'' or ''Reference Point'' case. An easy way to change the gas composition is to add water to the synthesis gas, if the water content is doubled the H_2/H_2O ratio will become 0.34 (figure 6B). Those calculations are denoted ''Double water''. An operation which is not so easy, in practice, would be to decrease the water content of the gas, the calculation with half of the normal water content, $H_2/H_2O = 1.4$ (figure 6C), is denoted ''Half water''. In the calculations, the hydrogen sulphide content in the gas phase has been varied between 0 and 200 ppm. The calculations are performed at an assumed inlet temperature of 350 ^{o}C and a pressure of 20 bars and the calculated values correspond to the inlet of the reactor. The gas phase composition varies along the reactor due to the reaction, and consequently the composition of the Fe-phase. Beside the inlet point, there is another fixed point that can be calculated, and that is from the point where the gas phase reaches the equilibrium state and to the exit of reactor. When forming hydrogen and carbon dioxide from water and carbon monoxide, the shift reaction is exothermal, due to the temperature increase the obtainable conversion is limited. For the ''Normal water'' case the maximum temperature has been calculated to 488 ^{o}C with the corresponding gas phase composition. With this gas composition the catalyst composition can be calculated in the same way as above. These calculations, the exit compositions, are shown in figures 6D–F. Different compounds that show up in the calculations are:

Fe, Fe_3O_4, FeO, FeS and Fe_3C

Fe_3O_4 and FeS are active in the shift reaction; however, the sulphide has lower activity than the magnetite. Inert compounds are Fe_3C and FeO.
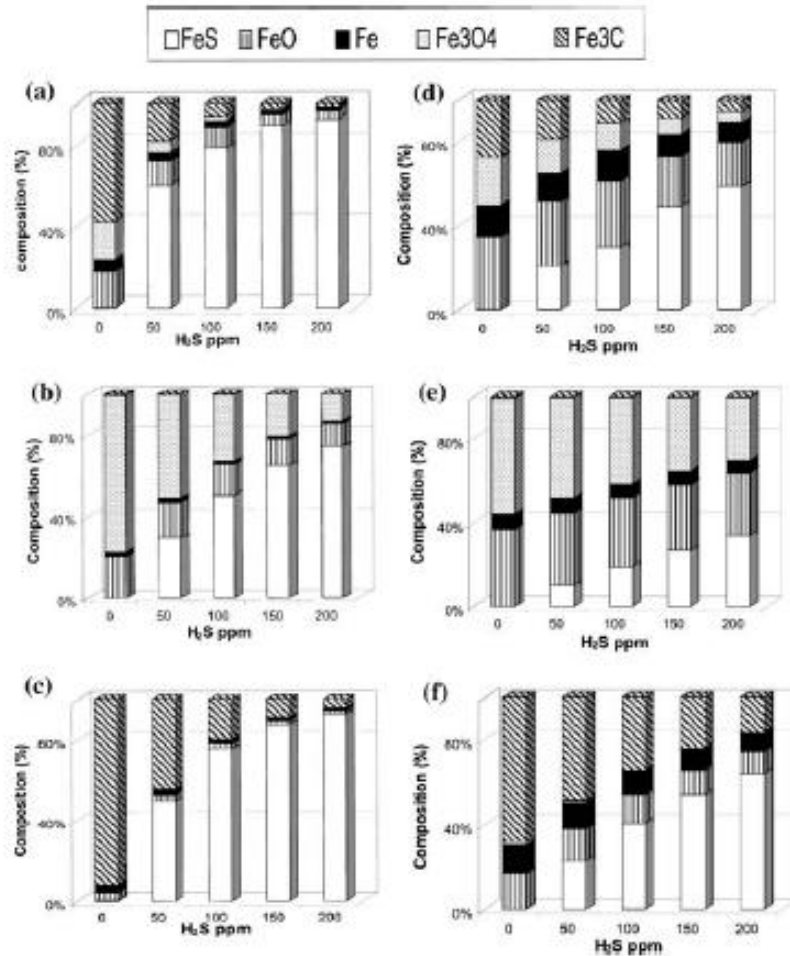
Figure 6.   (a) ''Normal water'', Catalyst composition at 350 ^{o}C and $H_2/H_2O = 0.7$
             (b) Double water, Catalyst composition at 350 ^{o}C and $H_2/H_2O = 0.34$
             (c) Half water, Catalyst composition at 350 ^{o}C and $H_2/H_2O = 1.4$
             (d) Normal Water, Catalyst composition at 488 ^{o}C and $H_2/H_2O = 0.34$
             (e) Double water, Catalyst composition at 488 ^{o}C and $H_2/H_2O = 0.7$
             (f) Half Water, Catalyst composition at 488 ^{o}C and $H_2/H_2O = 1.4$.

Formation of metallic iron (Fe) is considered negative since it can act as a Fischer-Tropsch or at least as methanisation catalyst. This could lead to re-formation of methane in the shift reactor, something that must be avoided.

Looking at the catalyst composition at the inlet, one can see that without sulphur present, carbide formation is significant in the Normal and Half water cases, the catalyst will probably not work particular well under these conditions. Doubling the water content eliminates the carbide formation entirely and suppresses the metallic Fe formation. The water content in the Normal water case without sulphur is too low to keep the catalyst in an active form and water must probably be added. When sulphur is present, the situation is improved, with sulphur levels above 100 ppm the carbide and Fe formation is minor and the catalyst will probably also work in the Half water case. However, with water addition, the Double water case, there will be a substantial formation of magnetite probably giving a better catalyst performance. The same observations are valid for the exit of the reactor as well; addition of water suppresses the carbide and Fe formation and increases the magnetite and sulphide formation. Compared with the inlet, the ratio of metallic Fe in the exit of the reactor is much larger and this might cause problems.

5. Undesired reactions

With increased pressure, there are risks for undesirable reaction paths, for instance methanisation and Fisher-Tropsch reactions. This will be the case if metallic iron is formed, and the reaction condition must be chosen to avoid the risks for such unselective operation of the catalytic reactor. In the best case an unselective operation might counteract the reformer and produce new hydrocarbons from the synthesis gas. In the worst case the presence of a more exothermal reaction than the shift reaction could cause a thermal runaway.

6. Conclusions

The calculations show that carbide formation is favourable in the ''Normal water'' case without sulphur in the gas. If sulphur is present in the gas, the situation improves due to sulphide formation. However, increased water content, double water case, shows increased magnetite formation and suppression of carbide and elementary iron. The water content in the Normal water case is probably too low. Addition of water will probably improve the performance substantially decrease the re-formation of hydrocarbon, i.e. methane, in the HT shift step.

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