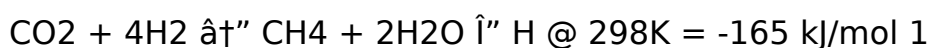
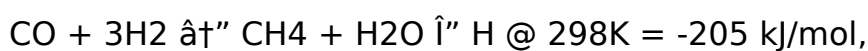


Methanation process of producing methane odourless colourless gas biology essay



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Introduction- What is methanation and how is it used? Methanation is the process of producing methane (CH₄) from H₂ and CO. Methane (an odourless and colourless gas, composed of four hydrogen molecules attached to one carbon molecule) is found in natural gas that we can use in our homes for energy. Methane found in natural gas is produced by anaerobic bacteria, which break down organic material and the waste product is the natural gas. The natural gas that is sought after by companies such as BP drilling for oil and gas was produced by anaerobic bacteria millions of years ago. Methane is used in many processes some of which are explained below. We will mainly consider methanation in the production of Substitute Natural Gas (SNG) as this can be used instead of natural gas which has limited resources and supply.



Methanation in the production of ammonia

Methanation is the reverse reaction of steam methane reforming. It is one of the most important steps in ammonia plants as the CO_x produced in the overall steam reforming process need to be separated from the H₂, as the H₂ is to be used for ammonia synthesis. This process is also referred to as 'purification' methanation. The content of oxides of carbon in the production of ammonia must be reduced to a very low level to prevent catalyst poisoning². After the low temperature shift (LTS) reaction and deduction of CO₂, the methanation reaction is used to remove any residual CO_x from the process stream before ammonia synthesis. Trace amounts of CO and CO₂

are reacted with hydrogen in the presence of a nickel oxide catalyst to produce a mixture of methane and water. This process removes the residual 0.2-0.5% CO and 0.1%-0.2% CO₂ to about 5ppm (it is vital to in the production of ammonia to remove the CO_x as even a low level significantly reduces the methanation rate) by reduction to methane with hydrogen in a fixed-bed reactor, with a 15-35 wt% Ni/Al₂O₃ catalyst (2). This catalyst is usually prepared by impregnating high surface area γ-Al₂O₃ with a soluble Ni salt. MgO can be used to impede sintering of the active Ni crystallites. For this process methanation is normally carried out in an adiabatic, fixed-bed reactor at 30 atm, with an inlet temperature of 300°C and an exit temperature of 365°C. This reaction is highly exothermic and the temperatures of the bed are kept below 400°C so that catalyst sintering and carbon deposition is prevented. 3

What is SNG?

Substitute/Synthetic Natural Gas (SNG) is similar to natural gas but produced from coal or biomass (e. g. wood, straw, waste). It is a manufactured product which is chemically similar to natural gas. Natural gas is the worldwide fuel of choice but there is limited supply, so SNG is one of the options to overcome this. Producing SNG from biomass is also considered to be thought of as 'green gas' as it avoids extra CO₂ emissions, because it is carbon neutral. SNG has many advantages some of which are:

the already existing gas supply infrastructure (e. g. pipelines) which allow the gas to be distributed throughout a country such as the USA and also worldwide

high conversion efficiency

Efficient final use technologies that are well-established e. g. Compressed Natural Gas (CNG cars), Combined Heat and Power (CHP), and Heating. 4

What is the methanation process and how is it used in the production of SNG?

$\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ The reaction between H_2 and CO can produce a number of different products depending on the reaction conditions, the catalyst used and the stoichiometry of the reactants. The reaction of great interest to us is the one producing methane. This reaction over a nickel catalyst was first reported by Sabatier and Senderens (1902, 1905) and even though a lot of research has gone into which catalyst is the best for methanation, nickel has continued as the key catalyst for methanation because of its selectivity for the production of methane, high activity, and inexpensiveness compared to other catalysts. Catalysts involved in methanation operate for a long time in catalyst beds and for that reason catalyst life and strength are also of major importance. Many problems such as sulphur poisoning are involved with these catalysts; they are mentioned in a later section of this report. 5

The above forward reaction is exothermic, releasing heat (the ΔH values are negative showing this) and the forward reaction is favoured by low temperature and high pressure, " Product gas with a high fraction of CH_4 can only be generated at low temperature (300-350°C) and high pressure > 20 bar." 6 We also know from Le Chatelier's Principle that pressure favours the

side with fewer moles which in this case is the forward reaction producing methane and water, so a high pressure should be used.

The production of methane is a fundamental step in the process of manufacturing that gas from coal to produce SNG. The typical methanation process involved in SNG consists of three fixed-bed methanating stages that are used in series with a fixed-bed of catalyst. A single stage process can and has also been used for methanation, such as the IRMA Methanation pilot plant KFA project, the conditions for this single stage were $P = 30$ bar; $T = 250-700^{\circ}\text{C}$ (1 stage); Volumetric flow rate = 600m^3 (STP) h^{-1} , (synthesis gas); 1100 operating hours since 19817. The three stage methanation process consists of:

Total Gasification of the coal in steam, possibly with oxygen, $\text{C} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}$

Changing the ratio of H_2 to CO in the product gas by the water gas shift reaction, and then removing any residual CO_2 . $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$

The hydrogen and carbon monoxide are converted to methane (following the removal of damaging material to the process such as hydrogen sulphide) using a catalyst (nickel is the most common for this process as explained later in this report.). This final stage is a straight through reactor operating at lower temperature than that of the previous stages as shown in Fig. 1 below. This gives methane which contains typically less than 3% H_2 , 0.1% CO and has a thermal efficiency of approximately 70% for the total process. This methane produced can then be use in the production of SNG. $\text{CO} + 3\text{H}_2 \rightarrow$

$\text{CH}_4 + \text{H}_2\text{O}$

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As the temperature needs to be controlled the product gases are recycled over the first stages with interstage cooling which prevents the temperature from increasing and also means that the process is more efficient as the gases are recycled and you don't have to put extra cooling in to keep the temperature from rising which saves money. The avoiding of high temperatures also protects the catalysts, " if the reaction temperature becomes too high not only is the equilibrium state of the hydrogenation reaction adversely affected but the catalyst life is shortened by sintering of the metal particles" 9.

Figure 1 (B. HOHLEIN, H. NIESEN, J. RANGE. (1984). Nuclear Engineering and Design. Methane from synthesis gas and operation of high-temperature methanation pg 2)

Fig. 1 shows the three-stage process with fixed-bed reactors and the corresponding thermodynamic equilibrium temperatures for the synthesis gas with 10% CH₄ at stage one and the desired dry product gas with more than 80% CH₄. This diagram also shows that after the first stages the temperature decreases again and this is to avoid high temperatures in order to protect the catalyst but also to reach thermodynamic equilibrium at low temperatures. This is done by product gas recycling cooling as explained before.

It is also important to know that when producing SNG by methanation the CO and H₂ (i. e. the reactants) will contain a lot more of the monoxide than in the methanation process used for ammonia synthesis. In ammonia synthesis only a small amount of monoxides (less than 1%) are found however in SNG

production the methanation process reactants can have 30-50% of the monoxide. It is also important to know that in the ' purification' methanation even a low amount of monoxides can seriously deteriorate the methanation process by catalyst poisoning. 8

Fig. 2 - Coal (B. HOHLEIN, H. NIESSEN, J. RANGE. (1984). Nuclear Engineering and Design. Methane from synthesis gas and operation of high-temperature methanation pg 2)

This picture shows the process of coal gasification, and then the products being cleaned and readied for methanation. Gasification is simply the process of producing coal gas, a mixture of CO and H₂ which is known as syngas. This syngas can then be used in the methanation process producing SNG.

How methanation is used in industry

From the 1970s quite a few methanation processes have been developed which consist of fixed bed and fluidised bed methanation. Most of the methanation processes used in industry use fixed bed reactors (used for the methanation in ammonia production, described before) as they are the most common type of reactor used in industry for many reasons such as having the simplest multi-phase reactor configuration where the solid phase is stationary and complications arising from the second phases mixing mode are not present. 10 However, some processes use fluidised bed reactors also as " fluidized bed methanation presents the advantage of good heat transfer from the process gas side to the cooling medium and the advantage of particular simplicity when exchanging the catalyst in case of catalyst

poisoning or catalyst deactivation.”¹¹ The choice of the reactor also depends on the size of the reactor needed and the costs of setup and operating (does it need to be cleaned regularly or not as this costs money and stops production).

One of the biggest plants to make SNG from coal-derived syngas was started up in 1984; the Great Plains Synfuels Plant of Dakota Gasification Co. which cost \$2.1 billion was the only SNG plant of that scale operating in the world. The plant uses Lurgi GmbH gasifiers (a steel construction where around each time 8 tons of coal is fed into a compartment at its top, known as a coal lock, which is then sealed with a gas being fed into it ahead of the bottom of the lock opening to feed coal, in this plant the coal is Lignite which is 60-70% carbon, into the body of the gasifier, this builds up high pressure and the high pressure and temperature feed of steam and oxygen in the gasifier decompose the lignite to produce syngas). The syngas is then converted to SNG using DPT methanation catalysts. This plant produces approximately 153 million ft³/day of SNG which is piped throughout the US. This facility has also implemented CCS (carbon capture and storage) and as of the end of last year (31/12/2009) it has captured more than 17.4 million m. t. of CO₂.¹² As you can imagine \$2.1 billion is a lot of money and was worth even more in 1984 showing that using methanation to produce SNG is not a small venture but a major player in the search for more fuel as the world's gas and oil reserves are depleting. In 2009 the plant produced \$264.7 million worth of SNG out of total revenue of \$426.1 million. The operating costs for this plant (including maintenance) were \$38,504,111.¹³ This shows that the

investment of \$2.1 billion was a really good decision not only in terms of producing SNG from methane but also a really great business return.

FIGURE 3 “ DPTs methanation process is a refinement and further development of the Catalytic Rich Gas (CRG) process, which was first developed by British Gas Corp. in the late 1960s to convert naphtha into town gas. The process involves several methanator reactors in series, with heat recovered from the exothermic reaction ($\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$) used to raise high pressure superheated steam and to preheat the feed. Each reaction stage consists of a fixed bed of CRG catalyst operating adiabatically.” 12

However, new and more efficient processes are being implemented in industry, that especially focus on the conversion of biomass, such as the Milena process in the Netherlands. The ECN (Energy Research Center of the Netherlands) has developed a biomass gasification technology with high gas efficiency and a high methane yield which allows it to be used for gas-engine applications. This process has been given the name Milena, and the product gas can be upgraded to SNG and ECN has the ambition to turn this into large scale SNG production with an energy efficiency of 70%. This would be much needed as the Netherlands relies on 50% of its energy from natural gas (which is not renewable) so using SNG for biomass would be a substitute for this and the biomass is available in large quantities and it a lot cleaner and friendlier to the environment than natural gas. 14

The biomass has to be converted into SNG by gasification and then methanation (theses processes and their outlines have been mentioned

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before). This allows it to reach efficiency, say from wood, up to 65% (this efficiency is calculated from the chemical energy output of SNG compared to the chemical energy input of wood). Biomass (e. g. wood and straw) being used to produce SNG has the advantage over coal based SNG of being almost CO₂ neutral, without CCS. Production of synthetic natural gas (SNG) from coal and dry biomass. 4

Catalyst Used

The main catalysts that are used as methanation catalysts are nickel or nickel supported catalysts. This is because the key catalyst properties of nickel are excellent for methanation as it has long life, high activity, selectivity for the formation of methane in preference to other hydrocarbons and the low cost compared to other catalysts. One of the main disadvantages for nickel catalysts is the sensitivity to poisoning by sulphur, other catalysts are available that are sulphur-resistant and also catalyse the methanation reaction but these are much less active than nickel resulting in a slower rate of reaction.

For example, one manufacturer's catalysts are formulated on Ca aluminate base with the active nickel incorporated in a NiO/MgO solution, this leads to negligible nickel sintering. In catalytic methanation many promoters for nickel have been studied such as copper, zinc oxide, magnesia, iron, calcium oxide, chromia and alumina. What was found was that alumina, chromia and magnesia were the best promoters in terms of activity and thermal stability.

It was also found that for thermal and mechanical stability " the best of a number of NiO methanation catalysts on supports of Al₂O₃, a mixture of

Al₂O₃ and CaO, MgO, SiO₂ and Cr₂ O₃ was NiO-Al₂O₃ containing 35% NiO." <https://assignbuster.com/methanation-process-of-producing-methane-odourless-colourless-gas-biology-essay/>

15 Many other factors are taken into consideration when choosing the catalyst for the methanation process. These are explained below:

(i) Sulphur poisoning.

Sulphur poisoning causes the methanation catalysts, to become inactive, this is because the reactants have brought in an alien molecule and this sits on the active site, the reactants now have to compete with this poison for the active sites and this results in a loss of the active surface area therefore decreasing the rate of reaction. 10

(ii) Thermal stability.

This reaction is highly exothermic it is very important to make sure that the reaction temperature does not become too high because it affects the equilibrium state of the reaction unfavourably and the catalyst life decreases due to sintering of the metal particles, where the particles come together, decreasing the surface area compared to when no sintering took place, thus less reaction is obtained. As mentioned previously the reaction temperature for this reaction is 300°C-400°C for which the nickel based catalysts used are sufficient in terms of longevity and activity. But there are catalysts that are able to operate at higher temperatures than nickel based catalysts and these would be even more desirable as “ the higher the temperature at which the heat of methanation is released the more effectively can it contribute to overall thermal efficiency of the conversion process, for example of coal to SNG, it is also worthwhile to notice that at these higher temperatures the problem of sulphur poisoning decreases due to instability of the catalyst metal sulphide⁹. So why is it that in industry the use of catalysts that are <https://assignbuster.com/methanation-process-of-producing-methane-odourless-colourless-gas-biology-essay/>

suitable for operation at higher temperatures are not selected and for e. g. nickel catalysts are favoured? This is due to the fact that it is not always feasible to use the best catalyst for the process as it may cost too much to buy.

(iii) Coke formation and fouling

Carbon in its unreactive form, or as Ni_3C produced on the Nickel catalyst, causes a loss of catalyst activity⁹. The coke formed blocks the reactants from reaching the active sites and the fouling is caused by the reaction forming a by-product which then sits on the active site, masking it. It is possible to avoid the unwanted carbon formation in the manufacture of SNG by controlling the water gas shift reaction. This is the 2nd step shown in figure 2 previously.

The cost of nickel catalysts varies as the price of nickel fluctuates. The suppliers of these catalysts do not sell just a few kilograms of the catalyst they have a minimum orders quantity, e. g. 20 tons at the rate of \$15000-\$30000 per ton. An example of a Methanation catalyst used in industry is the SG-9701 (the name may be fancy but it is mostly nickel as shown in the table) produced by the global leader in catalysis, BASF who have found that although the catalysts operate at low temperature and show good conversion rates in the Methanation process, “ they eventually begin to age and lose their effectiveness”, that is why through their current research they have identified that “ Methanation Catalyst relies on the mature combination of nickel oxide technology on an alumina matrix. However, through careful control of composition and geometry and the addition of a Rare Earth

promoter, a number of performance improvements are achieved”, these improvements are temperature resistance and long mechanical life. “ BASF’s methanation catalyst also boasts a superior physical makeup reducing deterioration that can lead to increased pressure drop in the system” 16

For the future?

Another SNG project was decided upon in this April between ConocoPhillips and POSCO (a Korean steel-manufacturing company) in which ConocoPhillips’ E-Gas technology is being used with POSCO’s Gwangyang coal to SNG project. This facility has targeted production of 500, 000 m. t. of SNG; I will not go further with this project as the methanation technology to be used has not yet been announced and a new technology to produce SNG using petroleum coke (petcoke) (an advanced technology that captures and sequesters CO₂ emissions from an industrial source) is to be implemented with this at a further stage. 12

Hydromethanation-Peabody Energy and GreatPoint Energy Mass recently signed an agreement to produce SNG from coal, H₂ from coal and also CCS projects. These are wanted to be developed with Bluegas technology, which “ uses catalytic Hydromethanation to produce H₂ and SNG. The process is more efficient and cost effective than conventional gasification routes to SNG”. In the bluegas process a “ propriety catalyst is dispersed with the feedstock (coal, petcoke, or biomass), and the mixture loaded into the reactor. Pressurized steam is injected from below to fluidize the mixture, which reacts to form CH₄, CO₂, H₂ and CO.” 12

There is also a German-Austrian project that wants to produce methane from extra electrical energy that has been generated from solar or wind power and a process that combines methanation with electrolysis has been developed at the Center for Solar Energy and Hydrogen Research, Germany.

Conclusion

Methanation is a very important process especially in today's environment where we look to reduce CO₂ emissions further and producing SNG from biomass using the methanation process does this rather than using natural gas. Methane is used in the gas that provides our homes with energy and heating. We need to find even more efficient processes like the ones described above that use methanation to produce SNG.