Production of synthetic natural gas (SNG) from coal and dry biomass – A technology review from 1950 to 2009

Jan Kopyscinski, Tilman J. Schildhauer *, Serge M.A. Biollaz

General Energy Research Department, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

Abstract
SNG production from coal or biomass is considered again due to rising prices for natural gas, the wish for less dependency from natural gas imports and the opportunity of reducing greenhouse gases by CO2 capture and sequestration. Coal and solid dry biomass (e.g., wood and straw) have to be converted to SNG by thermo-chemical processes (gasification followed by gas cleaning, conditioning, methanation of the producer gas and subsequent gas upgrading). During the 1970s, a number of methanation processes have been developed comprising both fixed bed and fluidised bed methanation. Meanwhile several new processes are under development, especially with a focus on the conversion of biomass. While coal based systems usually involve high pressure cold gas cleaning steps, biomass based systems require, due to the smaller unit size, different gas cleaning strategies. Moreover, the ethylene content of a few percent, typical for methane-rich producer gas from biomass gasifiers, is a challenge for the long-term catalyst stability in adiabatic fixed bed methanation due to the inherent high temperatures.

This paper reviews the processes developed for the production of SNG from coal during the sixties and seventies and the recent developments for SNG production from coal and from dry biomass.

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4.2. SNG from biomass

4.2.1. Energy Research Center of the Netherlands (ECN)

4.2.2. Center for Solar Energy and Hydrogen Research (ZSW)

4.2.3. Paul-Scherrer Institut (PSI)

4.3. Announced commercial international SNG projects

5. Conclusion

Acknowledgments

References

This review focuses on the methanation processes developed for the production of SNG from coal during the sixties and seventies (mostly in US, Germany) and on the recent developments concerning new processes for SNG production from coal and from dry biomass via thermal gasification.

2. Technologies for the production of SNG from solid carbon sources

The production of SNG via a thermo-chemical process requires several conversion steps, as depicted in Fig. 1.

The first step is the gasification of the solid carbon source (coal, biomass) with steam and/or oxygen and the production of producer gas, a gas mixture containing mainly H₂, CO, CO₂, H₂O, CH₄, and some higher hydrocarbons and impurities such as sulphur and chlorine species. The composition of the producer gas is influenced to a large extent by the gasification technology, i.e., by the type of reactor, the gasification agent, and the operating conditions.

The subsequent fuel synthesis process defines the range of permissible gas compositions and the maximum level of impurities at the inlet; therefore gas cleaning and gas conditioning are crucial. Gas cleaning shall be understood as the unit operations in which the impurities and catalyst poisons (such as sulphur and chlorine) are removed from the producer gas. In contrary, gas conditioning summarises all processes in which component of the producer gas are converted in such a way, that the resulting composition is suitable for the main application (i.e., for the fuel synthesis). The most common conditioning steps are steam reforming and water shift gas reaction as shown in Eqs. (1) and (2).

\[
\text{C}_\text{a} \text{H}_\text{b} + x \text{H}_2 \text{O} \rightarrow x \text{CO} + (x + y/2) \text{H}_2, \quad \Delta H^\circ_R > 0 \quad (1)
\]

\[
\text{CO} + x \text{H}_2 \text{O} \rightarrow x \text{CO}_2 + x \text{H}_2, \quad \Delta H^\circ_R = -41 \text{kJ/mol} \quad (2)
\]

The fuel synthesis itself is a heterogeneously catalysed process. In the hydrogenation of carbon oxides to methane, so-called methanation, beside the water gas shift (Eq. (2)), two further independent reactions are important (Eqs. (3) and (4)).

\[
3\text{H}_2 + \text{CO} \rightarrow \text{CH}_4 + \text{H}_2 \text{O}, \quad \Delta H^\circ_R = -206 \text{kJ/mol} \quad (3)
\]

\[
2\text{CO} \rightarrow \text{C} + \text{CO}_2, \quad \Delta H^\circ_R = -173 \text{kJ/mol} \quad (4)
\]

If the stoichiometric ratio of the reactants H₂/CO is at least three or more, carbon monoxide reacts with hydrogen to methane and water after Eq. (3). However, producer gases from coal and biomass gasifiers have usually H₂/CO ratios between 0.3 and 2, which are too...
low for good CO conversion and long catalyst lifetime. By means of
the water gas shift reaction (WGS, Eq. (2)), the H₂/CO ratio can be
adjusted by converting CO with H₂O to CO₂ and additional H₂.

The Boudouard reaction (Eq. (4)) is also of great importance,
since carbon on the catalyst surface can be considered as a neces-
sary intermediate during the methanation reaction, but carbon can
also lead to catalyst deactivation by formation of carbon whiskers
or polymeric carbon deposits or by encapsulation of metal crys-
tallites [12–15].

Methane can also be formed by hydrogenation of carbon oxides
in two other reactions Eqs. (5) and (6). It has to be noticed that
these reactions can be described as a linear combination of Eqs.
(2) and (3).

\[
\begin{align*}
2H₂ + 2CO & \rightarrow CH₄ + CO₂ & \Delta H^0 = -247 \text{kJ/mol} \\
4H₂ + CO₂ & \rightarrow CH₄ + 2H₂O & \Delta H^0 = -165 \text{kJ/mol}
\end{align*}
\]

The water gas shift (Eq. (2)) and the reactions Eqs. (3)–(6) are
exothermic. The methanation with all its covering topics such as
thermodynamics, reactions mechanism, kinetics and deactivation
mechanisms has been investigated intensively since Sabatier and
Senderens found in 1902 that nickel and other metals (Ru, Rh, Pt,
Fe, and Co) catalyse this reaction [16]. Nickel was and is still the
material of choice, due to its selectivity, activity and its price. How-
ever, these catalysts are very vulnerable to catalyst poisons such as
sulphur species (e.g., H₂S, COS, organic sulphur) and chlorine. The
published results on the different investigated topics, e.g., thermo-
dynamics, reactions mechanism, kinetics, and deactivation mech-
nisms, are summarised in [17–20].

From the thermodynamic point of view, it can be concluded
that the methanation is favoured at low temperature and high
pressure. Operating at high pressure produces a large amount of
heat per volume compared to a low-pressure process.

The main industrial application of the methanation has been
the removal of traces of CO in H₂-rich gas is the higher amount
of exothermic heat of reaction. The major objectives in the devel-
opment of catalysed methanation reactor concepts were to achieve
efficient removal of that heat to minimise catalyst deactivation due
to thermal stress and to avoid a limitation in the methane yield due
to approaching the chemical equilibrium. Besides a few special
reactor concepts, two main reactor concepts have been proven
suitable for the production of synthetic natural gas: series of adia-
batic fixed bed reactors with intermediate and/or gas recycle cool-
ing and fluidised-bed reactors.

3. Earlier process development for SNG from coal

The period after the Second World War until the 1970s has been
known as the "golden age" in natural gas (NG) use of the United
States [31]. In 1950, NG provided approx. 17% of the total primary
energy consumption of the United States, and its use increased dra-
matically to 30% in the 1960s and 1970s [32]. In the 1960s, the US
government and industry were concerned of a possible shortage of
natural gas due to the increasing demand. The US imposed new
regulations for the usage and price of the natural gas [31] and,
more important, began investigations for the development of an
efficient methanation process to convert coal to synthetic natural
gas.

Most of the studies and experimental investigations in the
1960s were financed by and carried out in the United States. The
results have been published on the yearly Synthetic Pipeline Gas
Symposium in Chicago (1969–1978, United States) and in technical
reports for the Department of Energy (DOE).

The oil crisis in the 1970s intensified the development of lignite
cellulose gasification processes with SNG production. Besides the
United States also Germany and Great Britain [33,27] were in-
volved in the development and improvement of such processes.
A few demonstration and pilot plants were constructed during this

![Fig. 2. Lurgi process with adiabatic fixed bed methanation reactor, adapted from [34].](image-url)
period, but only one commercial SNG plant was erected. The Great Plains Synfuels Plant by the Dakota Gasification Company (North Dakota, United States) was commissioned in 1984 and has been producing 4.8 Mio m$^3$ SNG per day[34] ever since.

3.1. Fixed bed methanation

Fixed bed methanation reactors are state of the art as gas cleaning units in e.g., ammonia plants. They are used to eliminate small concentrations of CO by methanation in hydrogen-rich streams prior to ammonia synthesis to avoid catalyst deactivation. The removal of the heat of reaction is not a problem in these applications, given the heat capacity of large gas volumes involved. For the production of synthetic natural gas, however, the heat of reaction has to be considered, due to the high amount of CO in the syngas. In this case, several methanation reactors are connected in series with intermediate gas cooling or recycle of product gas.

3.1.1. Lurgi process

In the 1960s and 1970s, Lurgi’s coal gasification process, developed in the 1930s in Germany, was the only commercially viable technology applicable for the production of synthetic natural gas in pipeline quality. Lurgi developed a methanation unit including two adiabatic fixed bed reactors with internal recycle. One pilot plant was designed and erected by Lurgi and SASOL in Sasolburg (South Africa) and another pilot plant was erected by Lurgi and EL Paso Natural Gas Corporation in Schwechat (Austria). In the first pilot plant, the methanation process was studied by using a syngas side-stream from the Fischer–Tropsch plant[35]. The synthesis gas was produced in a commercial coal gasification plant, which included a Rectisol scrubber and a shift conversion. The second pilot plant converted synthesis gas from naphtha to methane. The methanation unit in these two pilot plants consisted of two adiabatic fixed bed reactors with internal gas recycle, see Fig. 2. The pilot plants were operated for 1.5 years with two different catalysts; first a commercial catalyst with 20 wt.% Ni/Al$_2$O$_3$ and second a special methanation catalyst developed by BASF with a high nickel content (G 1–85)[35]. The experiment with the first catalyst showed a fast catalyst deactivation. The second catalyst operated for 4000 h and reached the adiabatic equilibrium temperature of 450°C after 32% of the catalyst bed, see Fig. 3.

The experimental conditions and gas compositions for a typical run of the pilot plant with the second catalyst are summarized in Table 1.

During the experiments the influence of the H$_2$/CO ratio (2.0, 3.7 and 5.8), CO$_2$ content, H$_2$O content, C$_2$–C$_3$ content, sulphur content (0.02 mg/m$^3$ and 4.0 mg/m$^3$ H$_2$S) and temperature and pressure were investigated [35,36].

The effect of hydrogen sulphide is depicted in Fig. 4, where the conversion in 6.3% and 23.8% of the total catalyst bed is plotted versus the operating time. From 750 to 950 h the setup was run with the Rectisol scrubbing unit and a ZnO-bed, which decreases

### Table 1

<table>
<thead>
<tr>
<th>Feedgas</th>
<th>Fixed bed reactor R1</th>
<th>Fixed bed reactor R2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet</td>
<td>Outlet</td>
<td>Inlet</td>
</tr>
<tr>
<td>Temp. (°C)</td>
<td>270 300 450</td>
<td>260 315</td>
</tr>
<tr>
<td>Gas flow rate (wet, m$^3$/h)</td>
<td>18.2 96.0 89.6</td>
<td>8.2 7.9</td>
</tr>
<tr>
<td>H$_2$</td>
<td>60.1 21.3 7.7 7.7 0.7</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>15.5 4.3 0.4 0.4 0.05</td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>13.0 19.3 21.5 21.5 21.3</td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>10.3 53.3 68.4 68.4 75.9</td>
<td></td>
</tr>
<tr>
<td>C$_2$</td>
<td>0.2 0.1 0.05 0.05 0.05</td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.9 1.7 2.0 2.0 2.0</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 3.** Temperature profile for the first fixed bed reactor, adapted from [36].

**Fig. 4.** Effect of H$_2$S on methanation reaction in Lurgi methanator, adapted from [35].
the total amount of sulphur to 0.04 mg/m³ = m³ N and 0.02 mg/m³ = m³ N for H₂S. After 6.3% of the catalyst bed the conversion decreases from 0.5 to 0.46, while no change was determined after 23.8% of the bed. From 950 to 1230 h the ZnO-bed was bypassed and the conversion decreased linearly to 0.42 after 6.3% of the bed; again no change in conversion was detectable after 23.8% of the bed. In the third period from 1230 to 1380 h 4.0 mg/m³ = m³ N of H₂S was added to the synthesis gas. Here the conversion decreased dramatically from 1.0 to 0.78 after 23.8% of the bed and below 0.2 after 6.3% of the catalyst bed.

Eisenlohr et al. [35] stated: 150 h with 4.0 mg/m³ = m³ N of H₂S corresponds to one year operation with 0.08 mg/m³ = m³ N of total sulphur in the feed gas to the methanation.

After 4000 h the nickel surface determined by H₂-chemisorption decreased by approx. 50% and the nickel crystallite size increased from 40 to 75 Å [36].

Based on the results from Lurgi and Sasol, the first and only commercial SNG from coal plant (Great Plains Synfuels Plant) was commissioned in North Dakota (United States). The plant is operated by the Dakota Gasification Company and consists of 14 Lurgi Mark IV fixed-bed gasifiers followed by a shift conversion unit (1/3 of the total stream) and carbon dioxide and sulphur removal via Rectisol scrubbing, see Fig. 5. In the pressurised gasifier, 18.000 tons of lignite coal per day \( \left( \tfrac{d_p}{C_{25}} \geq 0.6–10 \ \text{cm} \right) \) are contacted in counter-current operation (updraft gasification) with oxygen and steam. The resulting producer gas (dry gas compositions see Table 2) is cooled and reaction water is condensed to raise process steam [37,38]. The oxygen is delivered by an air separation unit

Table 2
Dry producer gas composition from pressurized lignite gasification [38].

<table>
<thead>
<tr>
<th></th>
<th>Vol.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>38.6</td>
</tr>
<tr>
<td>CO₂</td>
<td>32.4</td>
</tr>
<tr>
<td>CO</td>
<td>15.4</td>
</tr>
<tr>
<td>CH₄</td>
<td>11.9</td>
</tr>
<tr>
<td>C₂ – C₄</td>
<td>0.8</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.7</td>
</tr>
<tr>
<td>Other (N₂)</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 3
Traces of hydrocarbons and sulphur after the Rectisol scrubbing in the pilot plant [36].

<table>
<thead>
<tr>
<th></th>
<th>ppmv</th>
<th>mg/m³ N</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₄</td>
<td>180</td>
<td>0.08</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>750</td>
<td></td>
</tr>
<tr>
<td>C₃H₆</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>C₄H₄</td>
<td>14</td>
<td>0.04</td>
</tr>
<tr>
<td>Total sulphur (H₂S, organic)</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>H₂S</td>
<td></td>
<td>0.04</td>
</tr>
</tbody>
</table>

Fig. 5. Simplified process flow diagram of the Great Plains synfuel plant, adapted from [34]. AVS = Antelope valley station power plant.

Fig. 6. Scheme of the TREMP™ process, adapted from [39,41].
consisting of molecular sieves and a cryogenic separation unit. After the Rectisol scrubbing only traces of hydrocarbons and sulphur compounds were found, Table 3 [36].

After the methanation unit, the product gas is compressed and dried, CO₂ is removed and the resulting SNG is distributed to end-users via the national gas grid. Since 1999, CO₂ from the gas upgrading stage of this plant has been used for enhanced oil recovery in a nearby oil field. In addition to SNG and CO₂, the following main by-products are produced in the plant: krypton, xenon and liquid nitrogen come from the air separation unit; naphtha, phenol and dephenolised cresylic acid are produced in the gas liquor separation unit. Ammonium sulphate is produced in the flue gas desulphurisation unit. An ammonia plant was added to produce fertiliser by using a slip stream of the process gas after the Rectisol unit [34].

The commercial plant in North Dakota has produced SNG in pipeline quality since the commissioning 1984 with an availability of 98.7% in over 20 years. It was designed to produce 3.54 Mio m³/day of synthetic natural gas. After 1992, the plant delivered up to 4.81 Mio m³/day of SNG, due to continuous process optimisation and de-bottlenecking [34]. The clean syngas after the Rectisol unit contains approximately 20 ppb of total sulphur compounds, which results a catalyst lifetime of about four years [34].

### 3.1.2. TREMP process (within the ADAM and EVA project)

In the 1970 and 1980s, the Kernforschungszentrum Jülich (Germany), the Rheinische Braunkohlewerke (Germany) and Haldor Topsøe (Denmark) investigated steam reforming of methane and methanation of the synthesis gas as a cycle process designed to store and distribute over long distance process heat from nuclear high temperature reactors (NFE project – nuclear long-distance energy transportation) [33]. The high reaction enthalpy of the steam reforming reaction (and its reverse reaction, methanation) was to be exploited for this purpose. Methane was to be steam reformed using nuclear energy and the synthesis gas transported via pipeline to a heat consuming site, where it would be reconverted to methane and water to close the cycle and to produce heat. Steam reforming was investigated in the bench-scale unit EVA I and the methanation in the bench-scale unit ADAM I (heat release of 0.3 MWth) for more than 1500 h [33,39]. The methanation plant ADAM I (Anlage mit Drei Adiabaten Methanisierungsreaktoren) consisted of three adiabatic fixed bed methanation reactors including recycle according to the TREMP™ process of Haldor Topsøe, see Fig. 6.

### Table 4

Operation parameters and gas compositions of ADAM I from March 1979 [33].

<table>
<thead>
<tr>
<th></th>
<th>Feed</th>
<th>R1 Inlet</th>
<th>R1 Exit</th>
<th>R2 Exit</th>
<th>R3 Exit</th>
<th>SNG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. (°C)</td>
<td></td>
<td>300</td>
<td>604</td>
<td>451</td>
<td>303</td>
<td>23</td>
</tr>
<tr>
<td>Press. (bar)</td>
<td>27.3</td>
<td>27.2</td>
<td>27.1</td>
<td>27.05</td>
<td>27.0</td>
<td>27.0</td>
</tr>
<tr>
<td>Gas (m³/Nh)</td>
<td>535</td>
<td>1416</td>
<td>1255</td>
<td>348</td>
<td>334</td>
<td>119</td>
</tr>
<tr>
<td>H₂ composition (vol.%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>65.45</td>
<td>36.88</td>
<td>20.96</td>
<td>8.10</td>
<td>1.77</td>
<td>3.11</td>
</tr>
<tr>
<td>CO</td>
<td>9.84</td>
<td>4.28</td>
<td>1.17</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>CO₂</td>
<td>8.96</td>
<td>6.13</td>
<td>4.46</td>
<td>2.07</td>
<td>0.95</td>
<td>1.67</td>
</tr>
<tr>
<td>CH₄</td>
<td>11.30</td>
<td>28.12</td>
<td>37.44</td>
<td>44.36</td>
<td>47.28</td>
<td>82.95</td>
</tr>
<tr>
<td>H₂O</td>
<td>-</td>
<td>19.19</td>
<td>29.82</td>
<td>38.84</td>
<td>43.06</td>
<td>0.10</td>
</tr>
<tr>
<td>N₂</td>
<td>4.4</td>
<td>5.41</td>
<td>6.15</td>
<td>6.64</td>
<td>6.93</td>
<td>12.16</td>
</tr>
</tbody>
</table>

Fig. 7. Temperature profile of the adiabatic fixed bed reactor from ADAM I plant, [39].

Fig. 8. Simplified process flow diagram for the HICOM process [44].
TREMP stands for Topsøe's Recycle Energy efficient Methanation Process and is a heat recovery concept, which produces high pressure superheated steam. The temperatures in the reactors range from 250 to 700 °C and the pressure up to 30 bar. The temperature profiles for the three fixed bed reactors of ADAM I are plotted in Fig. 7. Beside the reactor technology, also the catalyst (MCR-2X, MCR4) for the high temperature methanation is provided by Haldor Topsøe [40]. The catalyst was tested at 600 °C for more than 8000 h and the results of the hydrogen chemisorption showed a decrease of the active surface from 7 m²/g for a fresh catalyst to 2–3 m²/g [33].

The NFE-process cycle (EVA I + ADAM I) was demonstrated in 1979 for a continuous test-run of 550 h. The experimental parameters are summarised in Table 4. Until 1981 more than 1500 h of operation could be achieved [39].

In 1981, a process demonstration unit EVA II/ADAM II (heat release of ADAM II 5.4 MWth) was erected by Lurgi and operated for more than 10,150 h until the project was terminated in 1986 [42] as the development of the high temperature nuclear reactor technology was discontinued.

Haldor Topsøe still offers the TREM Process for the production of synthetic natural gas from synthesis gas [41].

### 3.1.3. Conoco/BGC process

In 1972 on the Westfield Coal Gasification plant (Scotland), the first worldwide demonstration plant had been accomplished, which has proven the complete process chain from coal to SNG. Here, the Continental Oil Company (Conoco; today: ConocoPhilips, United States) and the British Gas Corporation (BGC, Great Britain) developed a fixed bed, gas recycle, adiabatic methanation reactor. The methanation unit was added to an existing Lurgi fixed bed gasifier. The gas cleaning prior to methanation was a Lurgi-Rectisol purification unit. In August and September 1974, approx. 59 Mio m³/day of SNG was fed into the local natural gas grid, and represented up to 60% of the total gas grid [43]. No experimental data and flow sheets are found.

### 3.1.4. HICOM process

A further development of the British Gas Corporation was the HICOM process (formerly HCM) in which the shift and methanation are combined. With this direct route, a thermal efficiency of about 70% from coal to SNG was proposed [44] (not taking the energy effort for pure oxygen production into account). Here, the producer gas from the coal gasifier is cooled and desulphurised and then passed to the methanation unit, which is followed by CO₂ removal. Compared to the processes described above, the CO₂ is removed after and not before the methanation stage. Therefore, the CO₂ removal unit does not need to handle any sulphur compounds. The simplified process flow diagram of the shift/methanation unit is depicted in Fig. 8.

The purified gas is heated and saturated by means of hot water in a countercurrent flow packed bed. Then the syngas is passed through a series of fixed bed reactors. The temperature is controlled by recycle of cooled, equilibrated product gas. Excess steam is added to the first methanation reactor to avoid carbon deposition. However, the excess steam reduces the thermal efficiency and may cause catalyst sintering. A part of the product gas from the main methanation reactors is recycled and the other part is passed through one or more low temperature fixed bed methanation reactors. In the latter, the remaining CO and H₂ are converted to CH₄ and CO₂. Most of the heat released is used to generate high pressure steam, while the heat from the last methanation reactor is used to warm the saturation water.

A bench-scale reactor (12.5 mm diameter) was erected for screening of catalysts and process conditions. The pilot plant...
consisted of 37 mm diameter reactors in which long-term tests under near-commercial conditions were studied. Typical gas compositions and operating conditions of the pilot test are summarised in Table 5. Several test runs of up to 2000 h duration were carried out with catalyst pellets of 3.2 mm and 5.4 mm.

A semi-commercial scale plant was built at the Westfield Development Center (Scotland) in which 5300 m$^3$/h purified syngas from a British Gas/Lurgi Slagging gasifier could be converted to SNG. No further data on these commercial scale experiments were found.

### 3.1.5. Linde process

In the 1970s, Linde AG (Germany) developed an isothermal fixed bed reactor with indirect heat exchange. The cooling tube bundles are embedded in the catalyst bed as shown in Fig. 9. There were plans to use this kind of reactor for the production of SNG from coal-derived syngas as published in a theoretical report [45]. The reactor itself was thought to be able to produce steam from the heat of the exothermic methanation reaction. A part of the steam should be added to the syngas mixture to minimize the risk of carbon deposition as it is depicted in the process flow diagram of the Linde SNG process, see Fig. 10. The syngas mixture should be then introduced into the isothermal and adiabatic methanation reactor. There was also the possibility to feed a part of the resulting product gas of the isothermal reactor into the adiabatic reactor to increase the methane yield. The product gases of both reactors are finally mixed, cooled, and reaction water is condensed.

No information is found whether or not Linde used the isothermal reactor concept to produce SNG from synthesis gas. By this, also no information about the temperatures and catalyst are found. Today, the Linde isothermal reactors are in operation in methanol synthesis plants.

### 3.1.6. RMP process

A high temperature methanation without gas recycle and no separate shift conversion unit (RMP process) was proposed by the Ralph M. Parsons Company (United States). The methanation process is depicted in Fig. 11 [46,47] and consists of 4–6 adiabatic fixed bed methanation reactors in series with intermediate gas cooling. The clean syngas could be added in different distribution ratios into the first four reactors and steam was fed into the first reactor. The system pressure was varied between 4.5 and 77 bar, the inlet temperatures of the reactors were varied between 315 and 538 °C and the H$_2$/CO ration was varied between 1 and 3.

The following Table 6 shows the dry gas composition and the temperatures of an experimental run at 27 bar. 40 % of the total cleaned syngas with H$_2$/CO ratio of 1 entered the first reactor together with steam with an inlet temperature of 482 °C. The product gas was cooled, then mixed with 30% of the syngas and fed to the second reactor. The last 30% of the syngas were added in the third reactor together with the product gas from reactor two. The inlet of the fourth, fifth and sixth reactors were temperature controlled as shown in Table 6. In the first reactor, CO was mainly converted to CO$_2$ by the water gas shift and minor the CH$_4$.

Water and carbon dioxide are removed from the product gas leaving the sixth reactor and fed to final dry methanation stage to reduce the hydrogen and carbon monoxide content below 3 and 0.1 vol.%, respectively.

### Table 6

<table>
<thead>
<tr>
<th>Syngas R1</th>
<th>R2</th>
<th>R3</th>
<th>R4</th>
<th>R5</th>
<th>R6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. (°C) (inlet)</td>
<td>–</td>
<td>482</td>
<td>538</td>
<td>538</td>
<td>538</td>
</tr>
<tr>
<td>Temp. (°C) (outlet)</td>
<td>–</td>
<td>773</td>
<td>779</td>
<td>773</td>
<td>717</td>
</tr>
<tr>
<td>Press. (bar) (outlet)</td>
<td>27.3</td>
<td>26.7</td>
<td>25.6</td>
<td>24.6</td>
<td>23.6</td>
</tr>
<tr>
<td>Syngas (vol.%) (inlet)</td>
<td>–</td>
<td>40</td>
<td>30</td>
<td>30</td>
<td>–</td>
</tr>
<tr>
<td>Syngas (vol.%) (outlet)</td>
<td>1.20</td>
<td>0.88</td>
<td>0.56</td>
<td>0.43</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Dry gas composition, vol.% at the outlet

<table>
<thead>
<tr>
<th>Syngas</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>R4</th>
<th>R5</th>
<th>R6</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>49.80</td>
<td>53.53</td>
<td>48.07</td>
<td>43.09</td>
<td>36.90</td>
<td>22.86</td>
</tr>
<tr>
<td>CO</td>
<td>49.80</td>
<td>13.97</td>
<td>18.46</td>
<td>20.63</td>
<td>15.25</td>
<td>5.64</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.10</td>
<td>25.80</td>
<td>24.04</td>
<td>23.64</td>
<td>29.21</td>
<td>39.90</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.30</td>
<td>5.70</td>
<td>9.43</td>
<td>12.64</td>
<td>18.64</td>
<td>31.60</td>
</tr>
</tbody>
</table>

Fig. 11. Fixed bed methanation in the RMP process [47].

Fig. 12. ICI high temperature once-through methanation process [30].
No data about the catalyst and the dimension of the reactors and were published and after 1977 no more information about this project can be found in the literature.

3.1.7. ICI/Koppers process

Similar to the RMP process, the former ICI (Imperial Chemical Industries, Great Britain) developed a catalyst and a high temperature once-through methanation process. This process aimed to produce SNG from the producer gas of the Koppers–Totzek coal gasifier [30]. The process consisted of three adiabatic fixed reactors in series with intermediate gas cooling as depicted in Fig. 12.

The inlet temperature of the first methanation reactor was set to 400 °C and the amount of steam was added in such a way that the temperature did not exceed 750 °C. The gas compositions and temperatures of an experimental run are given in Table 7.

The developed catalyst had a high nickel load (nickel oxide ~60%) and showed good activity, selectivity and physical strength in a test run for 1500 h. No large scale plant has been built.

### Table 7
Dry gas compositions and temperatures in the ICI methanation process [30].

<table>
<thead>
<tr>
<th></th>
<th>R1 Inlet</th>
<th>R1 Exit</th>
<th>R2 Inlet</th>
<th>R2 Exit</th>
<th>R3 Inlet</th>
<th>R3 Exit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. (°C)</td>
<td>398</td>
<td>729</td>
<td>325</td>
<td>590</td>
<td>300</td>
<td>428</td>
</tr>
<tr>
<td>Gas composition (vol.%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>42.9</td>
<td>35.5</td>
<td>35.5</td>
<td>20.3</td>
<td>20.3</td>
<td>5.8</td>
</tr>
<tr>
<td>CO</td>
<td>31.1</td>
<td>14.5</td>
<td>14.5</td>
<td>4.3</td>
<td>4.3</td>
<td>0.3</td>
</tr>
<tr>
<td>CO₂</td>
<td>24.7</td>
<td>40.2</td>
<td>40.2</td>
<td>53.9</td>
<td>53.9</td>
<td>62.7</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.1</td>
<td>8.5</td>
<td>8.5</td>
<td>19.8</td>
<td>19.8</td>
<td>29.1</td>
</tr>
<tr>
<td>N₂</td>
<td>1.2</td>
<td>1.4</td>
<td>1.4</td>
<td>1.7</td>
<td>1.7</td>
<td>2.0</td>
</tr>
<tr>
<td>H₂Oₐ</td>
<td>67.3</td>
<td>72.3</td>
<td>72.3</td>
<td>94.4</td>
<td>94.4</td>
<td>118.2</td>
</tr>
</tbody>
</table>

* Steam relative to 100 volumes of dry gas.

![Fig. 13. Scheme of the multiple-feed fluidised bed, from [21].](image-url)
3.2. Fluidised bed methanation

Fluidised-bed reactors are known to be suitable for large-scale operation of heterogeneously catalysed reactions with high exothermicity. The mixing of the fluidised solids leads to almost isothermal conditions in the reactor, which allows simple and easy control of the operation. Heat and mass transfer is high compared to fixed bed reactors [48]. Further advantage is the possibility to easy remove, add and recycle catalyst continuously during operation. However, special attention should be paid to attrition and the entrainment of the catalyst particles.

3.2.1. Bureau of Mines

In 1952, the former Bureau of Mines (United States Department of the Interior) had started a program to produce pipeline quality synthetic natural gas from coal via gasification and methanation [21,49]. Within this research project, one fixed bed and two different fluidised bed (FB) methanation reactors were developed, which were operated in total for more than 1000 h. The first fluidised bed had a diameter of approx. 19 mm, a reactor length of 180 cm and a 6.4 mm finned in-tube baffle combined with thermocouples to disperse the catalyst and to measure the catalyst bed temperature. Within this conventional FB-reactor temperature differences of over 100 K were measured. For that reason, a fluidised bed with multiple feed inlets was built. The second unit consisted of a 25.4 mm ID bed with three gas inlets located at the bottom, 45.7 cm and 99 cm above the gas distributor see Fig. 13. Both systems were operated in a temperature and pressure range of 200–400 °C and up to 20.7 bar, respectively, and also in recycle mode with a ratio of up to four. For the experiments 300–400 cm³ of an iron and Raney-nickel based catalyst were used, which was equivalent to a catalyst bed height of 90–120 cm. Both catalysts had particle size distribution of $d_p$ 63–180 μm. The H₂/CO ratio of the feed gas varied between 1 and 3 and the superficial gas velocity was around 0.3–0.43 m/s. The results showed a good temperature control in the multiple-feed fluidised-bed reactor (see Fig. 14) and that nickel was superior to iron as a methanation catalyst. The iron catalysts were not active enough to produce SNG in pipeline quality; the conversion of H₂ and CO was less than 80%, and in addition, higher hydrocarbon C₂+ and C₃+ were formed. The nickel catalyst was found to be very active and suitable for methanation of syngas, but extremely vulnerable to sulphur poisoning. Different types of nickel catalysts were used in the fluidised bed experiments.

The multiple-feed fluidised bed reactor was operated for approx. 1120 h with temperatures of 370–395 °C and a conversion of H₂ and CO of 95–98%, including two catalyst regeneration cycles. The first regeneration was carried out after 492 h, after the heating value of product gas dropped from 33.5 to 31.4 MJ/m³. For the regeneration, the catalyst was discharged and re-activated again by alkali extraction. The second run lasted about 470 h and the third run about 165 h [49]. The synthesis gas used in all the experiments was obtained by steam reforming of natural gas. It was afterwards compressed, passed through an activated char-coal trap, and finally stored in gas cylinders. The total sulphur content after the char-coal trap was approx. 0.23 g/m³. After the final report from Greyson et al. (1955) [21] and Schlesinger et al. (1956) [49] no more information about this project has been found.

3.2.2. Bi-Gas project

The Bi-Gas project was initiated in 1963 by Bituminous Coal Research Inc. (BCR, United States) with the aim of producing SNG from coal. The coal was converted in an entrained flow gasifier with oxygen and water. The entrained flow gasifier consisted of two stages: In the upper stage, pulverised coal was fed and reacted with steam and hot gas from the lower stage to synthesis gas and char. The char was completely converted with oxygen and steam in the lower stage, producing the heat for the upper endothermic stage. The temperatures in the lower and upper stages were about 1540 and 927 °C, respectively. The resulting producer gas was quenched, shifted and stripped of CO₂ and H₂S. After the acid gas...
removal, the synthesis gas was fed into catalytic methanation reactor [50]. The process flow diagram is depicted in Fig. 15.

The methanation reactor developed within the Bi-Gas project was a gas–solid fluidised-bed reactor including a second feed inlet and two in-tube heat exchanger bundles, as depicted in Fig. 16 [51,24]. The reactor had a diameter of approx. 150 mm with a reaction zone of 2.5 m height. It contained approximately 3 m² of internal heat transfer surface. The gas inlet zone was cone-shaped and surrounded by a cooling jacket. The coolant used for that application was a mineral oil.

A couple of test runs which lasted typically 5–10 days were carried out in a temperature range of 430–530 °C with a pressure of 69–87 bar and a catalyst charge of 23–27 kg. More than 2200 h were accumulated with the fluidised bed methanation system. The feed gas for the pilot experiments was prepared by steam reforming of natural gas followed by a water gas shift to adjust

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**Fig. 16. Fluidised bed methanation reactor by Bituminous Coal Research Inc. [24].**
the H2/CO ratio between 1.4 and 3 and removal of CO2 and H2S. The reactant gas consisted of 59 vol.% H2, 19 vol.% CO, 20 vol.% CH4 and some CO2, H2O and N2. The minimum fluidisation velocity of the catalyst was around \( u_{mf} = 0.3 \) cm/s and the normal superficial gas velocity was in the range of 2.4 and 5.5 cm/s, or 8–18 time \( u_{mf} \). The published results of the experiments showed that the conversion of CO was between 70 and 95%, [24,52,53]. The relatively low conversion means the product gas needed to be converted in a final fixed bed methanation reactor.

Furthermore, a catalyst-sampling device was added to the pilot plat, located in the middle of the catalyst bed closed to the intermediate gas inlet. About 100 g of catalyst were withdrawn at each sampling. By this, the catalyst size distribution was determined after different operating times. It was found, that the amount of fines was increasing while the amount of coarse catalyst particles was decreasing during the first few hours of fluidisation. Afterwards the catalyst reached a constant size distribution, which remained almost constant during 160 h [52]. The catalysts were delivered by the former Harshaw Chemical Company and contained nickel, copper, and molybdenum on an alumina support [54]. Besides the catalyst, also gas from the middle zone of the fluidized bed could be sampled and analysed. The conversions of the two zones were calculated for different ratios of the introduced feed gas. In the first case 100% of the feed gas was introduced at the bottom, in the other runs up to 40% of the feed gas was introduced in the intermediate gas inlet. The results showed that most of the CO was converted within the first part of the bed (96–99.2%), see Table 8. The catalyst seemed also very active towards the water gas shift reaction, which lead to high amounts of CO2 in the product gas. In the BCR methanation research project simultaneously water gas shift and methanation have been carried out in the same reactor; this concept was patented in 1973 [55].

Cobb and Streeter (1979) [53] derived from these experiments a simple kinetic approach in a form of a power law, with first order in CO. Furthermore, Cobb developed a two-phase fluidised bed model and calculated the conversion of CO at the outlet of the reactor. Due to the intermediate gas inlet and different temperatures along the height, the model considered the reaction zone as a series of three fluidised beds. No information has been found whether the fluidised bed methanation reactor had ever been operated with real synthesis gas from the Bi-Gas entrained flow coal gasifier. After the last publication in 1979, no more reports on the Bi-Gas project have been found in the literature.

### Table 8

Calculated CO conversion of the lower and upper zone of the BCR fluidised bed [52].

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Period</th>
<th>Zone</th>
<th>Temp. (°C)</th>
<th>Feed ratio</th>
<th>H2/CO</th>
<th>CO feed m³/h</th>
<th>CO conversion to (mol%)</th>
<th>Total CO conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Lower</td>
<td>418</td>
<td>100</td>
<td>3.1</td>
<td>15.3</td>
<td>69.2</td>
<td>96.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Upper</td>
<td>398</td>
<td>–</td>
<td>29.5</td>
<td>0.6</td>
<td>15.7</td>
<td>23.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lower</td>
<td>452</td>
<td>81</td>
<td>2.8</td>
<td>11.0</td>
<td>86.6</td>
<td>99.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Upper</td>
<td>433</td>
<td>19</td>
<td>4.5</td>
<td>2.6</td>
<td>57.7</td>
<td>96.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lower</td>
<td>478</td>
<td>60</td>
<td>2.9</td>
<td>12.2</td>
<td>88.3</td>
<td>98.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Upper</td>
<td>468</td>
<td>40</td>
<td>3.4</td>
<td>8.1</td>
<td>70.0</td>
<td>97.0</td>
</tr>
</tbody>
</table>

Between 1975 and 1986, the Thyssengas GmbH (Germany) and University of Karlsruhe (Germany) focused on a fluidised bed methanation reactor to produce SNG from coal gasification derived syngas in pipeline quality [56,26,27]. A pilot plant reactor with a diameter of 0.4 m was erected by Didier Engineering GmbH (Germany) and operated for several hundred hours between 1977 and 1981, see Fig. 17. The scheme of the so-called Comflux process and the experimental conditions are illustrated below, Fig. 18 and Table 9.

Later in 1981 a pre-commercial plant with a diameter of 1.0 m was erected, which contained between 1000 and 3000 kg of catalyst (\( d_p \) 10–400 \( \mu \)m). The description and commissioning of this plant is summarised in detail in a technical report by the Thyssengas GmbH [26]. The Comflux process was demonstrated on this industrial scale (2000 m³\( _{SNG}/h \); up to 20 MW\( _{SNG} \)) at the site of Ruhrchemie Oberhausen (Germany) [26]. 20 MW\( _{SNG} \) means the chemical energy content of the synthetic natural gas flow. The process was run with cleaned syngas with a stoichiometrically adjusted H2/CO ratio. In specific pilot scale experiments, it was shown that the isothermal operation allows the methanation of synthesis gas with a H2/CO ratio of 1.5 by addition of steam (combining the water gas shift reaction and the methanation in one apparatus).

In commercial plants, the omission of the shift unit and the product gas recycle compressor as well as the possibility to raise all steam at the same high pressure level should lead to significantly reduced investment and operation costs. With that project, the developers aimed at SNG cost 10% lower than from a fixed bed process [26]. The technology development was discontinued when the price of oil dropped in the mid of the 80s.

For this project, the University of Karlsruhe investigated the deactivation mechanisms of the catalyst [57,58], the kinetics of the reaction, the attrition resistance of the catalysts [59], the influences of sulphur on the methanation [60], and the deactivation due to carbon deposition for different nickel catalysts. For these investigations, a bench-scale unit with diameter of 52 mm and a height of 1000 mm was erected; see Fig. 19 [27].

The axial temperature profile for the empty reactor (\( \Delta \)) shows a huge temperature gradient, due to the different set temperatures, \( T = 275^\circ C \) for gas inlet and discharging zone and 510 °C in the reactor zone. The second curve (○) illustrates the temperature distribution during the methanation reaction at 408 °C. The temperature for gas inlet and discharging zone were set to 285 and 270 °C, respectively and the reactor was cooled with air. The catalyst mass in the reactor was 750 g and the gas velocity 0.2 m/s with a stoichiometrical gas mixture H2/CO = 3.

### 3.3. Other concepts

#### 3.3.1. Synthane projects

The Pittsburg Energy Technology Center (PETC, United States) developed in the 1970s in the framework of the Synthane project a catalytic tube wall reactor, an adiabatic parallel-plate methanation reactor and a hybrid reactor; the last two with gas recycle [61–66].

The tube wall reactor was essentially a tube whose inside or outside wall had been coated with Raney-nickel (42 wt.% Ni, 58 wt.% Al) with a thickness of 635 ± 50 \( \mu \)m. The proposed advan-
Advantages were removal of the heat by conduction through the wall to an organic liquid coolant and the very small pressure drop across the reactor. The feed of the syngas for the experimental tests of the methanation reactors was prepared by steam reforming of natural gas including two desulphurisation steps. Experiments of a few thousand hours using three different bench-scale reactors with gas stoichiometries of H$_2$/CO = 3–3.3, a wall temperature of approx. 390 °C, a pressure of 20 bar, and a gas recycle ratio from 0.5 to 3 were carried out [66]. After 1980 no more information about this type of reactors and the Synthane project have been found.

3.3.2. Catalytic coal gasification

Exxon Research and Engineering Company (United States) developed the catalytic coal gasification (CCG) process for direct...
production of synthetic natural gas as depicted in Fig. 20 [25]. The process consists of a low temperature fluidised bed gasifier with an acidic salt of potassium catalyst, and water, recycled hydrogen and carbon monoxide as gasification agent. However, due to the thermodynamic equilibrium, full conversion is not possible at 700 °C. Therefore, an amine scrubber and a cryogenic distillation at −150 °C was to separate products (methane, CO₂, water, ammonia, H₂S) and unconverted reactants (H₂, CO) that were sent back to the reactor. A bench-scale reactor with 15 cm inner diameter and 91 cm length was built and the catalyst recovery was demonstrated by long duration tests (up to 23 days of continuous operation). In the early 80s a process development unit was erected in which 1 ton of coal per day were converted to SNG [67].

3.3.3. Liquid phase methanation
Yet another way to produce SNG was proposed by Chem System Inc., (United States); to remove the heat of reaction efficiently, a
A three-phase fluidised bed methanation reactor was developed as depicted in Fig. 21, [68,69]. Syngas produced in a coal gasifier was introduced into the catalytic liquid phase methanation reactor (LPM) along with a circulating process liquid (mineral oil), which absorbs the heat of reaction. The product gas was separated in a liquid phase separator and in a product gas separator. The process liquid was pumped through a filter to remove any catalyst fines and recirculated back to the LPM reactor. The product gas, mainly methane and carbon dioxide with some unconverted hydrogen and carbon monoxide was analyzed and sent to a flare. No gas recycle was needed.

Table 10

<table>
<thead>
<tr>
<th>reactor type</th>
<th>BSU</th>
<th>PDU</th>
<th>Pilot plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor diameter (cm)</td>
<td>2.0</td>
<td>9.2</td>
<td>61.0</td>
</tr>
<tr>
<td>Reactor height (m)</td>
<td>1.2</td>
<td>2.1</td>
<td>4.5</td>
</tr>
<tr>
<td>Gas flow, (m³/h)</td>
<td>0.85</td>
<td>42.5</td>
<td>425–1534</td>
</tr>
<tr>
<td>Catalyst bed height (m)</td>
<td>0.3–0.9</td>
<td>0.61–1.8</td>
<td>–</td>
</tr>
<tr>
<td>Catalyst mass (kg)</td>
<td>–</td>
<td>–</td>
<td>390–1000</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>20.7–69</td>
<td>34–52</td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>250–380</td>
<td>315–360</td>
<td></td>
</tr>
<tr>
<td>H₂/CO</td>
<td>1–10</td>
<td>2.2–9.5</td>
<td></td>
</tr>
<tr>
<td>Catalyst size (mm)</td>
<td>0.79–4.76</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>
Experiments with different nickel catalysts (Harshaw, Engelhard, CCI and Calsicat), process liquids and operational conditions (260–360 °C, 20.7–69 bar, H₂/CO ratio 1–10, adding water) in three different reactors were carried out, see Table 10 [68,69]. The bench-scale unit (BSU) and process development unit (PDU) were operated for several runs of 40–80 h each. Furthermore, two long-term tests of 1400 h in the bench scale were carried out [70].

During the period of March 1977 to June 1978, in total more than 300 h of methanation were achieved on the pilot plant. The results showed low conversion and high catalyst loss from the fluidized bed reactor. A detailed report about the pilot plant operation was prepared for the US Department of Energy in 1979 [71]. The LPM-project was terminated in November 1981 [72].

4. Recent developments of SNG from coal and biomass

Since about ten years, SNG production from coal and biomass has been considered again, due to rising prices for natural gas and the wish for less dependency from natural gas imports and for a renewable alternative to NG (in case of biomass).

4.1. SNG from coal

Especially the United States has shown considerable interest in the coal to SNG process, because they have abundant coal resources, which will last for more than 220 years [1]. Converting these domestic resources to natural gas could satisfy the demand for natural gas and thus stabilize the energy market. The second advantage of converting coal to SNG is the generation of a concentrated CO₂ stream as by-product from the gas cleaning and/or fuel-upgrading step without additional costs associated with the CO₂ separation while in coal fired power stations, the CCS technology and the connected efficiency losses have to be added on top.

In the low-carbon economy, carbon management via carbon capture and sequestration (CCS) will be crucial and an important factor for economic evaluation of the SNG process. The CO₂ can be stored in non-atmospheric reservoirs (e.g., deep underground geologic formations or deep ocean).
4.1.1. Great point energy

Great point energy (United States) has been developing the so-called hydro-methanation (bluegas™) process aiming at carrying out coal gasification and methanation in one apparatus containing a catalyst at temperatures between 600 and 700 °C. This process resembles the Catalytic Coal Gasification process by Exxon; however, no further technical details on temperatures, catalyst composition, degree of conversion, product/reactant separation etc. can be obtained. Test campaigns operating for more than 1200 h have been carried out in the (leased) pilot plant of the Gas Technology Institute in Des Plaines (Illinois, United States) but no reports have been available so far [73].

4.1.2. Research Triangle Institute

The Research Triangle Institute (RTI, United States), has been developing a system for producing SNG and electricity from lignite or sub-bituminous coals. In the proposed process, coal is initially pre-processed in a transport pyrolyser to convert the coal into a mixture of gaseous carbon species, hydrogen, and solid char fines. The char is utilized to generate electricity, and the gaseous effluent from the transport pyrolyser is upgraded to a methane-rich syngas in a catalytic methanation fluidised-bed reactor. Sulphur species, ammonia, and CO₂ remaining in the syngas will be treated in gas clean-up steps to produce a clean SNG [74,75]. So far, no experimental results have been reported.

4.1.3. Hydrogasification process

The Arizona Public Service (APS, United States) [76] focuses on the so-called hydrogasification process in which coal will be gasified with hydrogen at moderate temperatures (870 °C) and high pressures (70 bar). The methane containing syngas is directly produced in the gasifier without any catalyst.

In the process proposed by APS, the syngas should be dried, cleaned, compressed, and the SNG should be injected into the natural gas pipeline. The unconverted char from the gasifier should be incinerated with pure oxygen to produce electricity and CO₂. However, for this process it is necessary to convert a part of the SNG back to hydrogen by steam reforming.

![Fig. 24. Result of long duration methanation test using PSI’s 10 kWth fluidised bed methanation connected to a slipstream of the FICFB gasifier in Güssing, Austria [93].](image1)

![Fig. 25. Block flow diagram of the 1 MW_SNG process development unit (PDU) in Güssing, Austria converting wood derived producer gas to SNG applying PSI/CTU fluidised bed methanation, adapted from [95].](image2)
4.2. SNG from biomass

The use of biomass for the production of SNG is most interesting, because biomass is carbon neutral and above this, by CO₂ capture and sequestration, the carbon balance would be negative. The challenges of using biomass instead of coal arise on one hand due to the different chemical composition and different kind of impurities in the producer gas such as organic sulphur, and due to the smaller unit size, on the other hand.

4.2.1. Energy Research Center of the Netherlands (ECN)

The Energy Research Centre of the Netherlands (ECN) began 2002 with a thermodynamic study and flow sheeting analysis to investigate the feasibility of the SNG production of biomass [77]. Later, a general concept was proposed including biomass gasification in a dual fluidised bed gasifier (MILENA), gas cleaning, methanation and SNG upgrading. In 2003, ECN showed the principle of methanation of a purified, hydrogen enriched producer gas from a wood gasifier (WOB, predecessor of MILENA) in a fixed bed catalytic reactor during 150 h [78,79]. There are plans to connect an up-scaled wood gasifier to ECN’s warm gas cleaning technology OLGA (oil gas wash) and a subsequent hydrodesulphurization step that converts organic sulphur to H₂S. The latter shall be removed by a zinc oxide bed while a pre-reformer should convert olefins etc. prior to the foreseen fixed bed methanation step [80,81]. The ongoing activity focuses on the construction of an 800 kWth pilot plant; the process is depicted in Fig. 22.

4.2.2. Center for Solar Energy and Hydrogen Research (ZSW)

The Center for Solar Energy and Hydrogen Research (ZSW) in Stuttgart (Germany) has developed the so-called Absorption Enhanced gasification/Reforming (AER) process in order to produce a hydrogen-rich gas from biomass by low temperature gasification in a dual fluidised bed gasifier [82]. Recent activities have focused on the production of SNG from AER producer gas by fixed bed methanation over a commercial nickel catalyst in a molten salt cooled multi-tubular reactor [83], see Fig. 23. The inlet and outlet
gas composition of the first bench-scale test are summarised in Table 11.

4.2.3. Paul-Scherrer Institut (PSI)

At the Paul-Scherrer Institut (PSI, Switzerland), research has been carried out on converting (dry) biomass to SNG for about ten years. The conversion of wood to SNG is an idea promoted by Gazobois SA (Switzerland) since the early 1990s. PSI joined in fall 1999 the Swiss initiative initiated by Gazobois SA and Ecole Polytechnique Fédérale de Lausanne (EPFL, Switzerland). End of 2002, a preliminary study was successfully finished that recommended basic decisions on the gasification and the methanation technology based on theoretical and experimental investigations [84]. The Fast Internally Circulating Fluidised Bed (FICFB) gasification process developed at TU Vienna (Austria) [85], built by Repotec (Austria) and operated under commercial conditions in Güssing (Austria) since 2002 [86] was selected as the most promising gasifier for two reasons: (1) The producer gas is nearly nitrogen-free but methane-rich and is therefore considered as very suitable for methanation. (2) The producer gas from this industrial gasification power plant with high availability is used to run a 2 MWel gas engine and can be used for long duration slip stream testing in an industrial environment.

For the scale-up to industrial size, the proof of concept on lab-scale was the first step. The composition of the producer gas from the FICFB gasifier resembles strongly the composition of the Lurgi coal gasifier (see Table 2), but contains a significant amount of unsaturated hydrocarbons (about 3 vol.% of ethylene). This amount of unsaturated hydrocarbons is a strong challenge for the nickel catalyst in adiabatic fixed bed methanation, as massive carbon formation was to be expected at the inherent high temperatures [87]. Therefore, the Comflux fluidised bed methanation technology (see Section 3.2.3) was selected as a technology with optimum temperature control. The key experiments, which were carried out in Karlsruhe in the 1970s were repeated and a bench scale fluidised-bed reactor was connected to a slip stream of the FICFB gasifier during 120 h in 2003 [88].

Until the end of 2004, two 200 h long duration experiments were performed with a fully automated 10 kW_SNG scale reactor system that was designed and built at PSI and then transferred and connected to the gasifier in Güssing (Austria) [89]. Deactivation of the methanation catalyst was observed after approx. 200 h of operation. By evaluation and development of suitable catalyst sample characterization methods, it could be shown that organic sulphur species were the primary cause for the limited catalyst lifetime [90]. Moreover, in 2005 it was shown in a further experimental series on the 10 kW_SNG scale that improved sulphur removal increases catalyst lifetime.

In situ measurements of the axial gas phase concentration profiles in a bench-scale test rig showed strong carbon exchange processes between gas phase species and carbon species on the catalyst surface. It was found that carbon species on the catalyst surface can be removed in certain zones of the fluidised-bed reactor [91,92] whereas under fixed bed conditions, rapid deactivation by carbon deposition has been observed in the presence of olefins [87]. Therefore, both, a proper removal of organic sulphur compounds, and a thorough carbon management on the catalyst surface are necessary to control the catalyst deactivation.

In summer 2007, catalyst stability for more than 1000 h could be demonstrated on the 10 kW_SNG scale, Fig. 24. In the once-through methanation step, a high methane content of about 40% and very little CO amount was reached [93].

Based on these results, a 1 MW_SNG Process Development Unit (PDU, Fig. 26) has been erected by Conzepte Technik Umwelt AG (CTU, Switzerland) and Repotec Umwelttechnik GmbH and commissioned with support of the TU Vienna, PSI and Biomassekraftwerk Güssing within the European Union project Bio-SNG [94]. Here, 1 MW_SNG means the chemical energy content of the synthetic natural gas flow.

The PDU allows the demonstration of the complete process chain from wood to SNG including gasification, gas cleaning, methanation and gas purification in half-commercial scale, see Fig. 25 [95] and Fig. 26. Commissioning of the gas cleaning and the methanation step was completed in November 2008; in December 2008, the first time FICFB producer gas was converted to methane-rich gas in the PDU.

In March 2009, commissioning of the gas purification was completed; in April 2009, the first operation of the full process chain was achieved. In June 2009, the PDU was operated during 250 h at up to 1 MW_SNG, producing 100 m³/h of SNG in H-gas quality (Wobbe index = 14.0, HHV = 10.67 kWh/m³) [96]. The suitability of the gas as a fuel was demonstrated by feeding a CNG fuelling station.

4.3. Announced commercial international SNG projects

A number of international projects for gasification plants with SNG production are proposed, in preparation and scheduled to be in service in the years to come. Table 12 gives an overview about several coal to SNG projects in the US and China [75,97,98]. Most of them include CCS to enable the use of coal without full CO₂ emission. For the Kentucky Newgas and the Southern Illinois Coal to SNG Facility project, the TREMP™ methanation process is proposed. For all the other projects no information is available.

For biomass, only one commercial project in Sweden is proposed at present. In the Gothenburg Biomass Gasification Project,
so-called GoBiGas. Bio-SNG will be produced by thermal gasification of forest residues. In 2008/2009, a basic design was conducted. In late 2009 until beginning of 2010, the methanation process from PSI/CTU (Switzerland) connected to the Repotec FICFB gasifier in Güssing (Austria) will be evaluated as a promising technology. The project is split in two phases; in the first stage, a 20 MW_{SNG} plant is scheduled to be commissioned in 2012. The second stage (about 80 MW_{SNG}) is scheduled to be in operation 2016 [104,105]. In Switzerland, several feasibility studies have been conducted in the last years.

5. Conclusion

SNG production from coal or biomass is currently considered due to rising prices for natural gas and the wish for less dependency from natural gas imports. During the 1970s, a number of methanation processes were developed comprising both fixed bed and fluidised bed methanation. Both concepts allow for combining water gas shift and methanation reaction in the same apparatus to adjust the H_{2}/CO ratio. This leads to a high flexibility with respect to the composition of the feed gas. While fluidised bed methanation allows for isothermal operation due to the high heat transfer coefficients, the heat of reaction in fixed bed reactors usually is removed by a combination of intermediate and gas recycle cooling. Depending on the concept, this leads to a higher number of reactors, heat exchangers, etc. Concerning the catalysts (usually nickel based), the two concepts face different challenges: in fluidised bed operation, the catalyst has to be attrition resistant, while in fixed bed operation, sintering due to the higher reaction temperatures has to be taken care of.

Since about ten years, several new processes are under development, especially with a focus on the conversion of biomass. Due to the inherent geographical distribution of the biomass resources, the process concepts for the production of SNG from biomass have to consider the biomass logistics. As a result, either few big plants (>400 MW_{SNG}) are planned at sites to where biomass easily can be transported (e.g. harbours) or a higher number of smaller plants (<100 MW_{SNG}). While in big plants, down-scaled technology similar to that in SNG-from-coal processes could be used, in smaller plants, the traditional cold gas cleaning (Rectisol®, Selexol®) cannot be integrated due to efficiency and financial limitations. Therefore, simpler gas cleaning strategies have to be applied.

Moreover, the ethylene content of a few percent, typical for methane-rich producer gas from biomass gasifiers, is a challenge for the long-term catalyst stability in adiabatic fixed bed methanation due to the inherent high temperatures. Therefore, the ethylene has to be converted to less reactive species (e.g., by hydrogenation) upstream of the fixed bed methanation as suggested in the ECN process concept. In contrast, the PSI/CTU isothermal fluidised bed methanation technology enables catalyst stability without upstream ethylene removal or conversion due to internal regeneration of the catalyst as could recently be demonstrated in 1 MW_{SNG} scale.

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References
