EUROPEAN COMMISSION

Community Research

SEVENTH FRAMEWORK PROGRAMME

EUROPAIRS

Support Action

Co-funded by the European Commission under the
Euratom Research and Training Programme on Nuclear Energy
within the Seventh Framework Programme

Grant Agreement no. 232651
Start date: 01/09/2009 Duration: 21 Months

www.europairs.eu

Processes requirements for nuclear assisted coal liquefaction with CO2 recycling

Deliverable D132

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End-User Requirements fOr industrial Process heat Applications with Innovative nuclear Reactors for Sustainable energy supply

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End-User Requirements fOr industrial Process heat Applications with Innovative nuclear Reactors for Sustainable energy supply

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Document title	Processes requirements for nuclear assisted coal liquefaction with CO2 recycling
Author(s)	Jerzy Cetnar (AGH), Mariusz Kopeć (AGH)
Number of pages	
Document type	Deliverable
Work Package	
Document number	D132 – final
Date of completion	
Dissemination level	☒ Confidential (EUROPAIRS consortium and European Commission) ☐ The above + specific dissemination group: … ☐ Public
Document status	

Summary
Review of recent progress of R&D programs in coal gasification and hydrogen production methods was done in order to assess new possibilities for nuclear assisted coal liquefaction with CO2 recycle. Coal liqefaction requirements were described for both major apporaches – indirerect and direct coal liquefaction.
Possible schemes of nuclear cogeneration dedicated for coal processing with CO2 recycle have been explored taking into account recent innovations and progress in alternative nuclear systems, coal gasification and hydrogen production. Possible synergies has be identified and the research areas for effective technology coupling described.
As external hydrogen is needed in convering hydrogen deficient coal into liquid fuel the process requirements for hydrogen production with excluded carbon dioxide production were also described.

Revisions

Rev.	Date	Short description	First author	Task leader	Work package leader	Coordinator
00	19/08/2011		J.Cetnar	-	-	E. Bogush

Distribution list

Name	Organisation	Comments
P. Manolatos, Europairs Scientific Officer	*EC DG RTD*	
All Europairs members		

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INTRODUCTION

Although most liquid fuels used today are petroleum based, an alternative way based on technologies of chemical synthesis draws growing attention in recent years due to the increasing market price of crude oil. The fuel price increase is perceived as stable as a result of structural changes of available natural petroleum resources, thus giving reasonable hopes for costs of synthetic fuel to be competitive. Synthetic fuel is any liquid fuel obtained from coal, natural gas, or biomass. It is usually called shortly synfuel. The process involved in synfuel production is referred to as XTL where X can be C for coal G for gas or B for biomass as the initial feedstock; Coal-To-Liquids (CTL), Gas-To-Liquids (GTL) or Biomass-To-Liquids (BTL). Chemical synthesis that leads to liquid fuel production involves technology that was developed long time ago basing on coal. Coal is much cheaper than petroleum and much more abundant resource, therefore fuel synthesis based on coal can be attractive in many countries. Few challenges remain and some of them can be eliminated by modernisation of the technology applied. As coal is still a valuable and relatively cheap energy source in many countries worldwide, its utilisation in power production makes major contribution to CO2 emission. The current policy of CO2 emission reduction is concerned with development and future deployment of carbon capture and sequestration (CCS) technologies. These are expensive and yet to be proved safe on a massive scale. If that effort does not succeed, further coal utilisation will halt any significant progress in CO2 reduction. Abandoning coal utilization will not be possible or at least easy in countries without other energy or fuel resources, mainly due to political reasons. The existing situation can be changed if coal, instead of functioning mainly as fuel for power production, becomes a substrate for chemical synthesis to produce synthetic liquid fuel of good market price and immense demand. A necessary condition for the technology deployment is to eliminate CO2 emission in the process by applying CO2 recycling instead. In principle this solution is possible if one resorts to an external non-emitting heat source to support the process. A prospective candidate here is the high temperature nuclear reactor HTR that apart from power production can deliver heat to the industrial processes. The entire process is called nuclear-assisted coal liquefaction, several concepts of which are possible, based on existing conventional technology. Implementation of such a system will be possible upon matching technological constraints of an HTR with the chemical process requirements resulting in sufficiently good efficiency and economics. In this technology coupling the critical parameter is temperature. It influences chemical processes efficiencies which for most of them requires its high level whereas for HTR its required limitation for the sake of time required for development and validation of a save and reliable reactor. Therefore the major underlying constrain for NCTL coupling is to achieve it under a limited temperature that would allow application of available materials, preferably basing on stainless steal rather than expensive super-alloys.

1 COAL LIQUEFACTION

The use of coal in the production of liquid fuels has a long history of both research and application, with its beginnings in the interwar period. The over 50-year long recession, as well as the final abandoning of this method of liquid fuel production were a result of losing its economic and ecological competitiveness in relation to the methods based on oil. Nevertheless, the research on coal processing has been carried on, even with considerable financial outlays throughout all this period up until the present. The stimuli for that were the recurrent (mainly political) crises influencing the oil market and above all the increasingly visible perspective of using up oil resources and the involved expectations of gradually changing cost relations in favor of coal.

The basic question is if the existing and available technologies are appropriate economically and ecologically, as well as what the chances for the future are. Is it enough to just evaluate the available options and follow in the pioneers' footsteps, or is that the way to expose ourselves to serious problems and threats, possibly causing more damage than gains? Anticipating the arguments presented below, we want to state at the outset, that the traditional technologies of coal liquefaction are not optimal for a European county like Poland. There is, however, a big potential for their enhancement, using the effect of synergy with nuclear energy. The clue of the concept is the use of heat from a high-temperature nuclear reactor allothermal processing of coal and also for the production of hydrogen required in the process.

Thus a radical reduction in the use of resources can be made possible in relation to a ton of final product, at the same time reducing or completely eliminating CO2 emissions.

The history of coal liquefaction

The viability of commercial production of fuels from coal was verified a long time ago in Germany. In 1944 the production of synthetic fuels for the army in war was run in 27 plants supplying annually 4m tons, which covered 90 per cent of the total demand. In 18 plants the direct Bergius process [1] was applied, in the other ones – the indirect Fischer-Tropsch process [2]. The interest in the issue could be observed in other countries too, maybe not on such a scale as in Germany: until 1945 less productive installations had been run in Great Britain, USA and Japan. Also in Poland in the 1960s coal liquefaction was carried out in chemical plant in Oświęcim. USA also started "Synthetic Liquid Fuels Program" during World War 2 in 1944. This programme was continued after the war and it developed the Karrick process [3] – a low-temperature carbonization (LTC) invented in the 1920s - and also involved the Bergius process. At that time no one was concerned with CO2 emission, or air pollution. Giving up work on these technologies in the after-war period, however, was mainly due to economic reasons: cheap oil meant the production of synthetic fuels from coal was unprofitable and discovering its new resources in the Middle East made the hopes for the steady and low prices of this raw material realistic. The only country that counted on synthetic fuels was South Africa, where large and easily accessible resources of cheap coal were available and there was a risk of restrictions on the supplies of oil as a reaction to the policy of apartheid in this country. The construction of the first SASOL installation was finished in 1954, and the successful experience resulted in the successive decisions in the mid 1970s of building new plants SASOL 2 and SASOL 3, of total production capacity of 150,000 bpd (barrels per day)[4].

The revival of fuel synthesis

Rapid increase of oil prices in the world markets in the mid 2000s and the growing concern about its shrinking resources caused that the CTL process has gained a new perspective. The growing interest has appeared in the countries with large coal resources, but not enough oil. The major reason is the crude oil price level, which reached its peak about US$143,95 a barrel in July 2008, later to stabilise above US$60 in mid 2009. Such a level gives sufficient margin to make new CTL installations competitive. The production cost of synfuel is estimated to be around US$35 in the current USA economic conditions, however it is country dependent. At present the biggest investment is under way in China by Shenhua Group, where 8 pilot "clean coal" conversion plants have been constructed by 2010. Annual capacity of CTL stands at 1.68 million tons of fuel and is planned to reach 3 million tons of annual output by 2015. In parallel, other conversion routes are established - coal-to-gas with 15 billion cubic meters annual capacity and coal-to-olefin with 1.7 million tons annually [5]. The cost of the first stage of Shenhua project was estimated at US$3.3 bn and the predicted price of synthetic oil would be around US$15 pb. Following the Chinese example India [6], Indonesia [7] and Australia [8] are planning CTL installations with the fuel production capacity of 80,000 barrels a day. In USA over a dozen CTL projects were announced in the last decade, and some of them filed permit applications [9]. It should be noted that some of the projects were cancelled after facing challenges of environmental impact or financing the investment of US$4-5 billion.

It should be noted that some investments in synthetic fuel production actually concern gas-to-liquid process. Oryx GTL plant [10] in Qatar, co-owned by Qatar Petroleum and SASOL, produces 34,000 bpd. Also in Qatar, Shell is constructing the world largest gas-to-liquid plant – Pearl GTL Plant [11], with target capacity of 140,000 bpd. Shell's first commercial-scale GTL plant in Bintulu[12], Malaysia was constructed in 1993 with the capacity of 14,700 bpd. In Nigeria Chevron and SASOL are constructing GTL installation of 30,000 bpd production capacity to be operational in 2013[13].

The commercial use of GTL in New Zealand has been taking place since the 1980s using methanol-to-gasoline process - MTG. For economic reasons the MTG plant was taken out of production in late 1996 but a recent interest in CTL activities has renewed interest in MTG technology which can be applied here

instead of the Fischer-Tropsch process[14]. There is also wide interest in GTL use in the USA, where such plants have been started on a commercial scale.

Characteristics of conventional technologies of coal liquefaction

The hydrogen content in coal is comparatively low and does not exceed 6 per cent by weight, while in the liquid fuels it is at the level of 12.5 to 14.5 per cent. Thus processing coal to liquid fuels requires an appropriate increase of hydrogen content in the product, which can be achieved in two ways: either by removing some coal in carbonization or pyrolysis processes, or by adding hydrogen in liquefaction processes. The direct method (DCL) or the Bergius process consists in introducing hydrogen into carbon structures, initiating hydrogenation process, which is followed by upgrading and separation liquid hydrocarbons, while in the two-stage indirect method (ICL) or the Fischer-Tropsch process carbon is initially gasfied, and then from the mixture of CO and H2 liquid fuels are synthesized.

Since fuel efficiency of coal is lower than that of synthetic fuel the conversion process requires energy to cover the difference which can be obtained from summing up the enthalpy of all involved reactions. The overall energy required to carry out entire process is made up from the total enthalpy enlarged by the energy that is additionally used for preparing coal for processing, producing appropriate amounts of oxygen used in the gasification process or for producing hydrogen used in the direct methods. In conventional technology the involved technological processes are designed so as to use part of processed coal for the energy production. This results in excessive consumption of coal and enlarged CO2 emission. As a result, for one litre of synfuel 3 to 6 kg of coal are required, depending on the process and coal quality. Generally, direct process requires better quality coal with its lower consumption while F-T process is designed for lower quality coal but with higher consumption. At the same time the problem of large CO2 emission appears – almost tenfold in relation to oil processing with the same fuel output [15]. A way of its reduction considered worldwide is CO2 capture and sequestration. It consists in depositing the gas in appropriate geological strata underground. However, such a solution increases production costs and in some cases is not possible to implement. The doubts connected with its safety are not less important, when considering for example the catastrophe that occurred as a result of natural escape of CO2 in the vicinity of Nyos Lake in Cameroon in the summer of 1986. Thus it should be expected that the application of the existing technologies of synthetic fuels production from coal must involve serious consequences of ecological nature. It seems that in Europe, seriously considering the obligations in the Kyoto Protocol, this aspect alone might prove an insurmountable obstacle for such implementation of CLT concept. The determination of EU lawmakers has already been translated into binding regulations for European countries, introducing CO2 emission limits. Within the frame of the European Emissions Trading Scheme (EU ETS) installations are granted European Emission Allowances (EUA), which then are subject to trade. One EUA unit allows for emission of one tone of CO2. The market price in the beginning of 2011 was oscillating around €14.5 per EUA[16]. Price projections for the future have a rather wide uncertainty margin and depend on CO2 reduction goals yet to be taken by EU. In case of 20% reduction goal till 2020 it is expected to be at a range of €25-50 while for the more ambitious goal of 30% reduction - €35-65 per EUA, according to the Point Carbon company that specialises in the emission trade consultancy. The cost of emission adds significantly to the projected costs of synfuel production using conventional technology. The cost of one barrel of synfuel should be increased roughly by the cost of one EUA, which in recent trades is around US$20. With the expected EUA price increase by a factor of 2 to 4, the added cost for emission can reach US$80, which level would question economic viability of conventional approach.

2 INDIRECT COAL LIQUEFACTION

Indirect coal liquefaction allows to convert solid coal into valuable high quality liquid fuels in two steps:

- Coal gasification to syngas - a mixture of CO and H2. which contains also toxic gases thus needs a cleanup process
- Fischer Tropsch process (FT) of syngas carried out in a reactor with presence of a catalyst. The result is a mixture of liquid hydrocarbons, which are further refined to produce liquid fuels.

Coal gasification

The gasification occurs in a gasifier in which the coal carbon reacts with water steam and oxygen. Main gasification reaction are endothermic coal gasification:

$$C + H2O \rightarrow CO + H2 \qquad (\Delta H^{o}_{298} = 118.9\ kJ/mol)$$

and exothermic incomplete combustion:

$$C + \tfrac{1}{2}\, O2 \rightarrow CO \qquad (\Delta H^{o}_{298} = -123\ kJ/mol)$$

Water is used as steam and oxygen is injected either pure or as the air content. Application of air reduces the need for air separation unit (ASU) to produce oxygen but has a significant drawback in the significant increase of the gas volume to be treated and cleanup. Moreover, it results in production of nitrogen oxides NO and NO2.

Other important reactions – complete carbon combustion:

$$C + O2 \rightarrow CO2 \qquad (\Delta H^{o}_{298} = -406\ kJ/mol)$$

and water-gas shift (WGS):

$$CO + H2O \rightarrow H2 + CO2 \qquad (\Delta H^{o}_{298} = -40.9\ kJ/mol)$$

involve production of CO2 which should be definitely avoided in the first case as a waste of coal or accepted in the latter case as an additional source of H2 in the syngas. WGS can be in purpose enhanced in dedicated WGS reactors in order to match syngas component proportions according to FT process requirements. It should be noted that hydrogen in the syngas is also supplied directly form coal which is a solid hydro-carbon, after the gasification converts carbon into carbon oxides. Due to the presence of sulphur in coal and nitrogen in air, various highly toxic, corrosive, flammable or explosive gases are being produced: sulphur dioxide SO2, hydrogen sulphide H2S, carbonyl sulphide (COS) and nitrogen oxides NOx (when air is applied). They all need to be removed from syngas since they are poisons for the catalysts used in the FT process [15].

Gasifier technology

Available gasifier technology in industrial usage is based on auto-thermal processes where combustion is the source of heat. They offers quite large range of working temperature from 400 °C up to 1400 °C. The lowest temperature occurs in the Lurgi technology of fixed or moving bed gasifiers which is in use in Sasol's plants. However, in operating practice of Sasol Lurgi gasifiers the working temperature is about 1000 °C

[16]. Higher temperatures are applied in fluidized bed gasifiers (KRW) which allow very quick gasification of coal – up to 20 times shorter retention time than in the Lurgi technology, but its application is limited to the low mineral content coal. Application of oxygen allows for significant increase of temperature up to 1400 °C in entrained flow gasifiers (Texaco), which are dedicated for IGCC plants [17].

Gasifier temperature influences the retention time in reactor, in that the higher temperature the shorter time. This issue will become important for allothermal reactors where the heat transfer through the heat exchanger walls is considerably slower than in case of auto-thermal process. The coal type also matters. Experiments in Julich, Germany in '70 and '80 s for hard coal at 800°C the conversion reached 30%/h while for lignite 100%/h. Very important experience was gained in allothermal grassfires for coal, in which experimentally was proven that with the use of catalyst K_2CO_3 gasification temperature of 700°C results in sufficiently high conversion rates above 2% C/min obtained with caking coal as Fig. 1. shows [18].

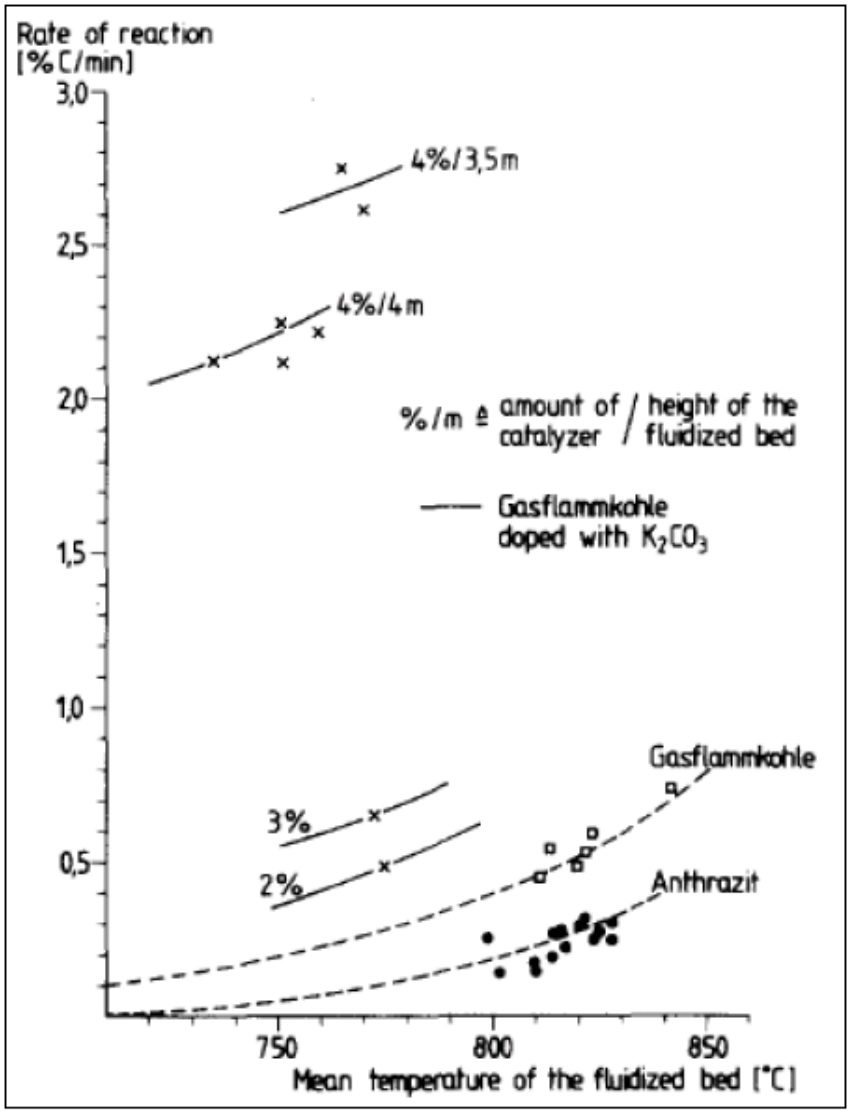

Fig. 1. Reaction rate of coal in Julich allothermal coal gasifier

In consideration what technology under what process condition would be most suitable for NCTL system with CO_2 recycling, a detailed experimental investigation must be undertaken in order to find solutions that minimise generation of CO2 under limited temperature. Here the Boudouard reaction:

$$C+CO2 \leftrightarrow 2CO \qquad (\Delta H^{\circ}_{298} = 159.7 \text{ kJ/mol})$$

favours with increased temperature the CO formation, which is desirable for CO_2 minimization, but the higher temperature may conflict the major underlying constrain for NCTL coupling. Compromise in this aspect need to be work out. Composition of gas leaving the allothermal gasifier shown on Fig. 2. points

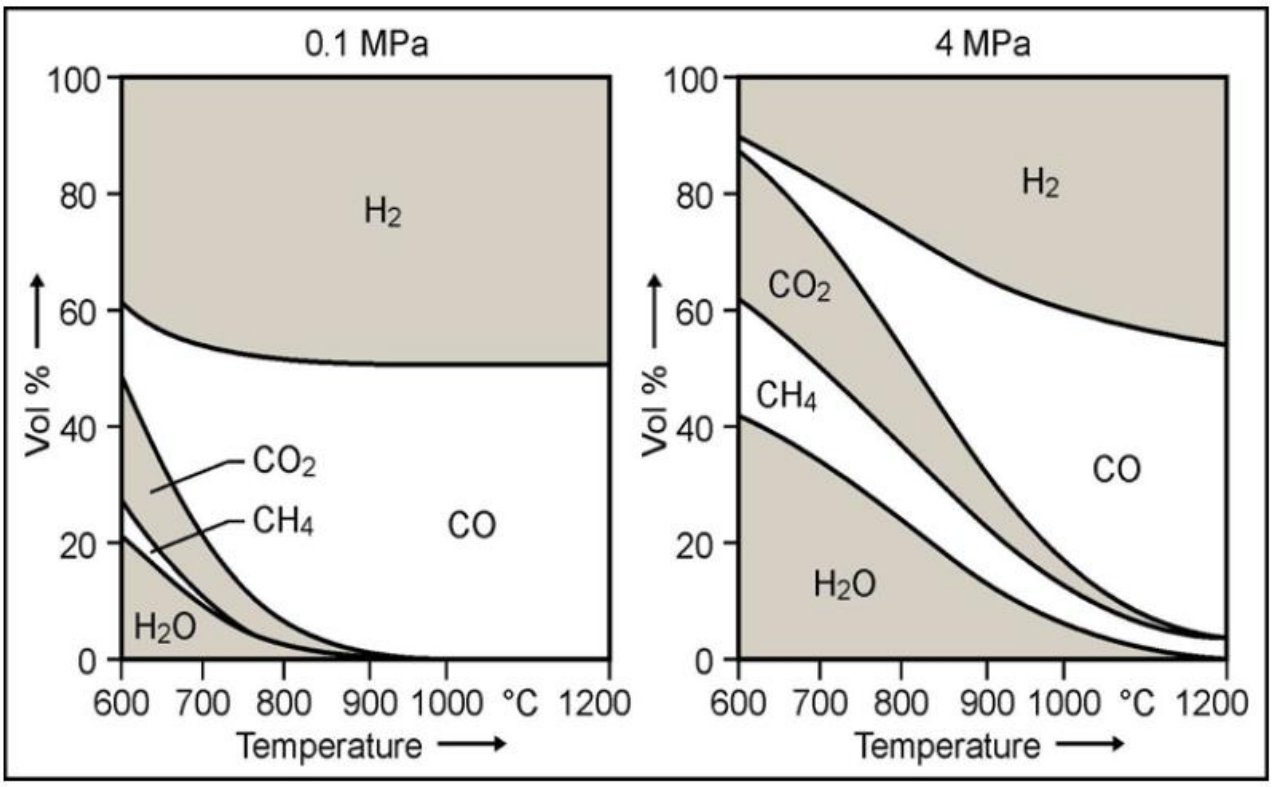

Fig 2. Gas composition after steam coal gasification in Julich allothermal coal gasifier

that in low pressure system even in temperature as low as 600°C substantial fraction of hydrogen is released. Question worth experimental investigation is how what would be the process output at 500°C concerning gas composition as well as formation of heavy fractions in form of slug.

As the aim of this analysis is synfuel production from coal with CO2 recycling, it is of minor importance for the balance of CO2 the composition of carbon gases in the outlet of allothermal gasifier, while no oxygen is used. For carrying out further the FT process one need to supply to the FT reactor the syngas of appropriate hydrogen to carbon ratio. Therefore other system components that convert CO_2 are needed and external supply of hydrogen or hydrogen rich gas – methane is needed. Required processes are available like dry methane reforming [19]:

$$CH4 + CO2 \rightarrow 2CO + 2H2 \qquad (\Delta H^{o}_{298} = 247.9\ kJ/mol)$$

or reverse water gas shift (RWGS):

$$CO2 + H2 \rightarrow CO + H2O \qquad (\Delta H^{o}_{298} = 40.9\ kJ/mol)$$

The raw syngas contains many contaminants, which must be removed before it is passed to a FT reactor. In this process the syngas flows through a liquid solvent, in which the contaminants are absorbed. Then the solvent releases the contaminants, which then are treated appropriately, while it is being heated or cooled down.

The Fischer Tropsch process

Fischer Tropsch process is carried out in a reactor with presence of a catalyst. The result is a mixture of liquid hydrocarbons, of the composition depending on the catalyst and the process conditions (temperature, pressure). The main reaction is the formation of saturated hydrocarbons (alkanes – know also as paraffins, which includes major components of liquid fuels like gasoline or diesel):

$$nCO + (2n+1)H_2 \rightarrow C_n H_{2n+2} + nH_2O$$

Other sellable hydrocarbon products are created as unsaturated hydrocarbons (alkenes– known also as olefins) C_nH_{2n} and alcohols $C_nH_{(2n+1)}OH$, but undesirable generation of CO_2 also occurs.

FT process is an exothermic reaction (39.4 kcal/mole of CO). Hence the syngas from gasifier as well as the reactor itself has to be cooled down. FT reactor dedicated for the final product as gasoline works usually with an iron based catalysts in temperature range of 330-350°C, whereas with a cobalt based catalysts and temperature of 200°C it will produce mostly diesel.

The gasification process requires heat in the range of steam class for steam production, coal preheating and syngas treatment. The chemical class steam would be required for curing out the gasification. FT reaction is exothermal therefore no external heat is required. The FT heat can be recovered in range of steam class in syngas cleanup process thus lowering demands for external heat of steam class.

3 DIRECT COAL LIQUEFACTION

Direct liquefaction processes add hydrogen to the hydrogen deficient organic structure of the coal, raising the H/C ratio from ~0.8 to ~2 allowing for production of distillable liquids. Many different processes have been developed, but most are closely related in terms of underlying reaction chemistry. Common features are the dissolution of a high proportion of coal in a coal-derived solvent at elevated temperature (~400°C) and pressure (15–30 MPa), followed by the hydrocracking of the dissolved coal with H_2 and a catalyst. Direct liquefaction is the most efficient route currently available. Liquid yields in excess of 70% by weight of the dry coal have been demonstrated for some processes. Overall thermal efficiencies for modern processes are generally in the range 60-70% if allowance is made for generating losses and other non-coal energy imports. The quality of liquid products from direct liquefaction processes is generally lower than from indirect processes and further upgrading is required before they can be used directly as transportation fuels.

Direct liquefaction processes can be divided into two main groups, depending on whether the initial dissolution of the coal is separated from the conversion of the dissolved coal into distillable products:

- **single-stage direct liquefaction process** – gives distillates via one primary reactor or a train of reactors in series. Such processes may include an integrated on-line hydrotreating reactor, which is intended to upgrade the primary distillates without directly increasing the overall conversion;
- **two-stage direct liquefaction process** – designed to give distillate products via two reactors or reactor trains in series. The primary function of the first stage is coal dissolution and is operated either without a catalyst or with only a low-activity disposable catalyst. The heavy coal liquids produced in this way are hydrotreated in the second stage in the presence of a high-activity catalyst to produce additional distillate.

Some processes were designed specifically to co-process coal with petroleum-derived oils and these may fall into either group. Also, coal liquefaction processes from both groups have been adapted for co-processing [20,21,22,23].

Single stage processes

The single-stage processes developed furthest are:

- Bergius (IG Farben, Germany)
- Kohleoel (Ruhrkohle, Germany)
- NEDOL (NEDO, Japan)
- H-Coal (HRI, USA)
- Exxon Donor Solvent (EDS) (Exxon, USA)
- SRC-I and II (Gulf Oil, USA)
- Imhausen high-pressure (Germany)
- Conoco zinc chloride (Conoco, USA).

In fact, most of these processes have been superseded and abandoned. Two exceptions are the Kohleoel and NEDOL processes, which are considered ready for commercialisation by their developers. Several other, less important, processes were developed to a modest scale in the USA, Russia and Poland (GIG process).

Two – stage processes

Most two-stage direct liquefaction processes were developed in response to the oil price rises of the early 1970s, often as a development of earlier single-stage processes. Work was carried out in many different countries, but relatively few processes were developed beyond the laboratory scale and many were generically very similar. Processes include:

- Catalytic Two-Stage Liquefaction (CTSL) (USDOE and HRI, now HTI, USA)
- Liquid Solvent Extraction (LSE) (British Coal Corporation, UK)
- Brown Coal Liquefaction (BCL) (NEDO, Japan)
- Consol Synthetic Fuel (CSF) (Consolidation Coal Co, USA)
- Lummus ITSL (Lummus Crest, USA)
- Chevron Coal Liquefaction (CCLP) (Chevron, USA)
- Kerr-McGee ITSL (Kerr-McGee, USA)
- Mitsubishi Solvolysis (Mitsubishi Heavy Industries, Japan)
- Pyrosol (Saarbergwerke, Germany)
- Amoco CC-TSL (Amoco, USA)
- Supercritical Gas Extraction (SGE) (British Coal Corporation, UK).

Most of these processes have been suspended and abandoned. Only the CTSL, LSE and BCL processes continued in development beyond the late 1980s.

Comparison of different DCL technologies

Contemporary DCTL methods work by pressures 15–30 MPa and temperatures 430–450°C. Depending on the particular method, the process often does not require catalyst. The consumption of coal is usually in the range 2–3 kg per 1 kg of liquid products, whereas the hydrogen consumption varies between 5 and 10%. These data are summarized in Table 1 [20,21,22,23,24,25,26,27]

Table 1. Comparison of DCL technologies

Process	Max. temp. [°C]	Max. pressure [MPa]	Catalyst	C cons. [kg C/kg prod. liq.]	H cons. [%]
Bergius	485	70	$FeSO_4$ $Fe(OH)_3$	2.1	9.9
GIG	450	20	No catalyst	2.4	4.7
Kohleoel	470	30	Fe_2O_3	2.0	10.5
LSE	430	20	Ni – Mo	2.0	no data
NEDOL	450	20	Ni – Mo	2.5	4.8
SCR II	440	20	FeS_2	2.5	5.0
EDS	480	15	No catalyst	2.2	7.5
CTSL	440	7	Ni – Mo	2.7	6.5
Shenhua	450	18	Multi.	2.1	5.5

Technological advancement of discussed methods is diverse. All of them have passed the laboratory and small scale demo phase (up to 10 t/d). Among the methods tested in middle demo scale (up to 150 t/d), which have been subsequently implemented in pilot plants are SCR (Morgantown), as well as LSE and NEDOL (Shenhua). For a few processes tested in a large demo scale (up to 250 t/d), eg. IGOR and EDS, the commercial installations have been designed, but they didn't enter construction phase. The Polish method GIG, despite of optimistic results obtained in a small scale, still must be tested in a larger scale (200 t/d). The project of such installation has been designed in early 90s, but is still waiting for implementation. Recently important progress can be observed in China, where on the basis of HTI, NEDOL and IGOR+ technologies a proprietary process has been developed.

Table 2. Research and development of direct liquefaction technologies

Process	Capacity [t/day]	Time
GIG	0.5 ; 2 ; 200 (project)	1967 – 1970; 1986 – 1991
Kohleoel	0.5 ; 200 ; 5000 (project)	1981 – 1987; 1997 – 1999
LSE	0.05 ; 4.5 ; 65 (project)	1983 – 1995
NEDOL	2.4 ; 50 ; 135	1996 – 1998
SCR II	6 ; 25 ; 50 ; 6000	1974 – 1981; 1989 – 1991
EDS	250 ; 22500 (project)	1979 – 1985
CTSL	2	1985 – 1988; 1997
Shenhua	6000	2007 – now

DCTL processes vs. other coal liquefaction technologies

Comparing to coal liquefaction technologies the DCTL processes have generally higher conversion ratios as Table 3. shows. The theoretical efficiency of DCL process can be as high as 70-75%. However, the only processes currently under consideration are expected to give 65-70% to finished fuels; 67% is thus a fair average figure for DL. Indirect liquefaction is much less efficient. Theoretically it can be 60-65%, but Sasol 1 shows only 37%. However, Sasol 2 and 3 are said to be much better, perhaps ~50%. Generally, the DCL efficiency is ~10% higher than the ICL one. The coal and hydrogen consumptions are also generally lower in direct processes. The standard coal may be converted to the syncrude by direct or indirect liquefaction at thermal efficiencies of 75% and 61% respectively, with all the carbon in the coal, not ending up in the syncrude, converted to CO_2 (either in power stations or furnaces). For direct or indirect liquefaction this amounts to 1.8 and 3.0 t-CO_2/t-syncrude respectively. It is important however, that CO_2 release in the whole DCL process is connected almost exclusively with H_2 production. Having better, low-emission or even emission-free hydrogen production methods, one could drastically reduce CO_2 emissions of DCL processes.

Table 3. Comparison of coal conversion technologies

Item		Unit*	Direct liquefaction	Indirect liquefaction		Methanol
				High temp.	Low temp.	
Technical efficiency		%	59.75	41.56	41.26	45.64
Products recovery		% daf	55.15	38.09	43.20	100.35
Resource use	Water	t/GJ	0.16	0.25	0.26	0.31
	Coal	t/GJ	0.061	0.075	0.076	0.068
Release to environment	CO_2	kgC/GJ	20.09	34.72	35.61	29.22
	SO_2	kg/GJ	0.01	0.004	0.004	0.003
	NO_x	kg/GJ	0.09	0.133	0.186	0.17
	Dust	kg/GJ	0.01	0.01	0.013	0.02
	Water	kg/GJ	6.87	6.29	6.46	5.58
	Residue	kg/GJ	3.36	9.92	10.29	8.86

4 THE USE OF HIGH-TEMPERATURE NUCLEAR REACTOR FOR COAL LIQUEFACTION

The main premises for using a high-temperature nuclear reactor for the production of synthetic fuels from coal come from the need to modernize this process, so that it is profitable in European conditions and at the same time fulfils the strict ecological requirements. Furthermore, such requirements have to be fulfilled not only now, but also in the future. In our opinion, the optimal solution is using the high-temperature reactors. Conscious of common fears of any system using a nuclear reactor, we consider a plant of highest safety standards – both in the operating sense and as to the proliferation of nuclear materials - as the only acceptable solution. Such reactors are designed and tested at the moment, and they can become available in the not-so-distant future, fulfilling all the requirements we postulate. Although the main reason stimulating the present work on the high-temperature reactors is the idea of using them for the production of hydrogen, nothing stands in the way of using them in the processes we are focusing on.

Economic and ecological aspects of the nuclear-coal synergy

Using an external heat source from a nuclear reactor will make it possible to use coal in an optimal way, treating it as a raw material for processing and not any longer as a heat source for the whole process. Thus, the fuel efficiency can reach a maximum – close to 100 per cent. Obviously, there will be a new item on the cost side – connected with the capital and operational costs of a nuclear reactor. In a time perspective, though, economic relations will favour such a solution, as a result of growing savings in the use of coal at its rising prices, but also through limiting the importance of the growing labour cost. Similarly, the cost of nuclear reactor installation will decrease in the future as a result of progress, modularity or its wider use. An important factor in the economic calculation is also a radical drop in the CO2 emission, which will make it possible to avoid high ecological tax, designed to increase in the plans of the EU lawmakers. An estimated cost of nuclear production of hydrogen from water in the conditions of US economy is below US$2 per kilo, some estimations go down even to the level of US$1.25 per kilo[**Erreur ! Source du renvoi introuvable.**]. An additional economic advantage is the by-production of oxygen, which counts as a significant cost in the traditional process, and is also responsible for a part of carbon dioxide emission.

As has been said before, production of liquid fuels from coal by use of the present versions of indirect processes involves the total CO2 emission at the level almost ten times higher than that in the refining process based on crude oil. On the other hand the synthetic fuels obtained have excellent properties from the point of view of ecological requirements. The low content of sulphur (below 1 ppm), nitrogen compounds, aromatic compounds, but also favourable performance parameters make it possible to enhance the engine operation conditions, at the same time limiting the emission of NOx, CO, CO2, hydrocarbons and particulate matter[18]. There is no doubt then, that the synthetic fuels themselves are ecologically desired. Serious problems occur only at the production stage. Basing the CLT processes on synergy with nuclear energy gives us a chance to limit the CO2 emission even to the level similar to that in the crude oil processing. Achieving such a situation would make it possible to lower the total emission from production and use of the fuels.
In the wider perspective, i.e. taking into consideration the energy sector and the changes due to happen in it, the necessity to reduce the CO2 emission to avoid paying fines is reflected in the strategic plans of Poland as the announced modernization of the sector and gradual adoption of nuclear power industry. In such circumstances coal industry is naturally looking for its chance by exploring new areas in coal application. Liquid fuel production from coal can be such an option, but only if the problem of CO2 emission is solved. The presented proposal is able to achieve this.

Guidelines for effective system integration with excluded CO2 output

High temperature technology is a research area of a very high difficulty and material requirements level. This is mainly due to the temperature range to be encountered in the industry using high temperature heat sources based on coal or hydrocarbon oxidation. The main factor limiting the development of this technology is the durability of construction materials, mainly steel, which in reality limits the temperatures to about 800oC. In spite of ambitious plans to raise this limit and the research in this area, no significant progress has been made. Recently observed realignment of working parameters of HTR reactor results in lowering helium temperature at the reactor output to about 800oC and recommending substitution of an IHX heat exchanger with a steam generator[28]. Due to this realignment the evaluation of technological maturity as well as economic efficiency of water splitting through thermo-chemical S-I process have been changed – mainly due to high-temperature requirements, but not only. This makes it difficult to implement the simplest way of nuclear-coal synergy - through nuclear supported water hydrolysis and recycling of carbon dioxide into a hydrocarbon (indirectly through RWGS). At the same time one should bear in mind the requirement of eliminating carbon dioxide emission in the process of its gasification or liquefaction, as a necessary condition of the feasibility of the process, due to legal regulations. Geological sequestration of carbon dioxide should not be treated as an option, as the key motivation for nuclear-coal synergy is exactly an alternative for sequestration. In spite of the limitations mentioned above the nuclear-coal synergy can be implemented in another way. That is using methane to produce hydrogen through pyrolysis or steam or carbon dioxide (dry) reforming processes in allothermal version (with an external heat source for the process). Similarly, we should use allothermal coal gasification, which will decrease its oxidation and carbon dioxide production. As a target, all carbon dioxide will be recycled and the need for sequestration – eliminated. Technological challenges will involve: coupling nuclear energy processes with conventional ones, providing for appropriate heat transfer efficiency, the choice of catalysts lowering the process temperature, the choice and thermal improvement of materials, enhancing their resistance to degrading, etc. Integration options of coal liquefaction system should be studied in order to minimise CO2 generation and ultimately exclude its output to the environment. CO2 once is generated requires introduction of high enthalpy to brake its bound, therefore we should avoid as much as possible generation of it applied processes. Basic reason for which CO2 is generated is heat requirement, therefore substitution of carbon combustion heat source for an external one is highly desirable. From other side of coal liquefaction process requirements results the need of hydrogen, which can be also produced in water shift process that generates CO2 and does not required high temperature – which is needed for water splitting. Having in mind existing limitation of available technology of HTR as a heat source, an entire elimination of CO2 generation might not be possible at near future, but still by involving hydrogen rich methane one can still develop the process with excluded CO2 output.

To achieve this major goal one should follow the following guidelines:

- Apply nuclear heat as much as possible within proven range of temperatures (T< 800^{o}C)
- Assess option of hydrogen from methane reforming
- Lower the process demands for hydrogen – the most costly energy carrier
- Reduce the CO2 generation as much as possible and favour the generation of CO
- Convert CO2 into CO using heat (nuclear or conventional waste heat)

Ways of system integrations: nuclear - water splitting – coal – synfuel

We can consider two different approaches to the system integration that will affect the technology readiness level and the process efficiency. The efficiency is always welcome but often requires substantial R&D effort and thus affects the technology readiness level. The two different ways of system coupling described below – loose and tight - visibly show different features.

Loosely coupled system

It is characterised by the following features:

- water splitting or methane pyrolysis is achieved by nuclear or off-peak electricity
- oxygen (if generated) is supplied to the coal systems
- hydrogen and CO2 are supplied to chemical systems (for fuel synthesis)

Its advantages are:

- Easiness of coupling
- Early realization possible
- Possible retrofitting of conventional technology
- Can serve for technology demonstration

Its disadvantages are:

- Limited efficiency due to high cost of conventional electrolysis
- Cost of methane, R&D needs for methane pyrolysis

Tightly coupled system with water splitting

It is characterised by the following features:

- It is integrated on the process level as much as possible
- Thermo-chemical water splitting with application of both nuclear and conventional heat source is applied
- It involves gasification process with suppressed CO2 production or recycle

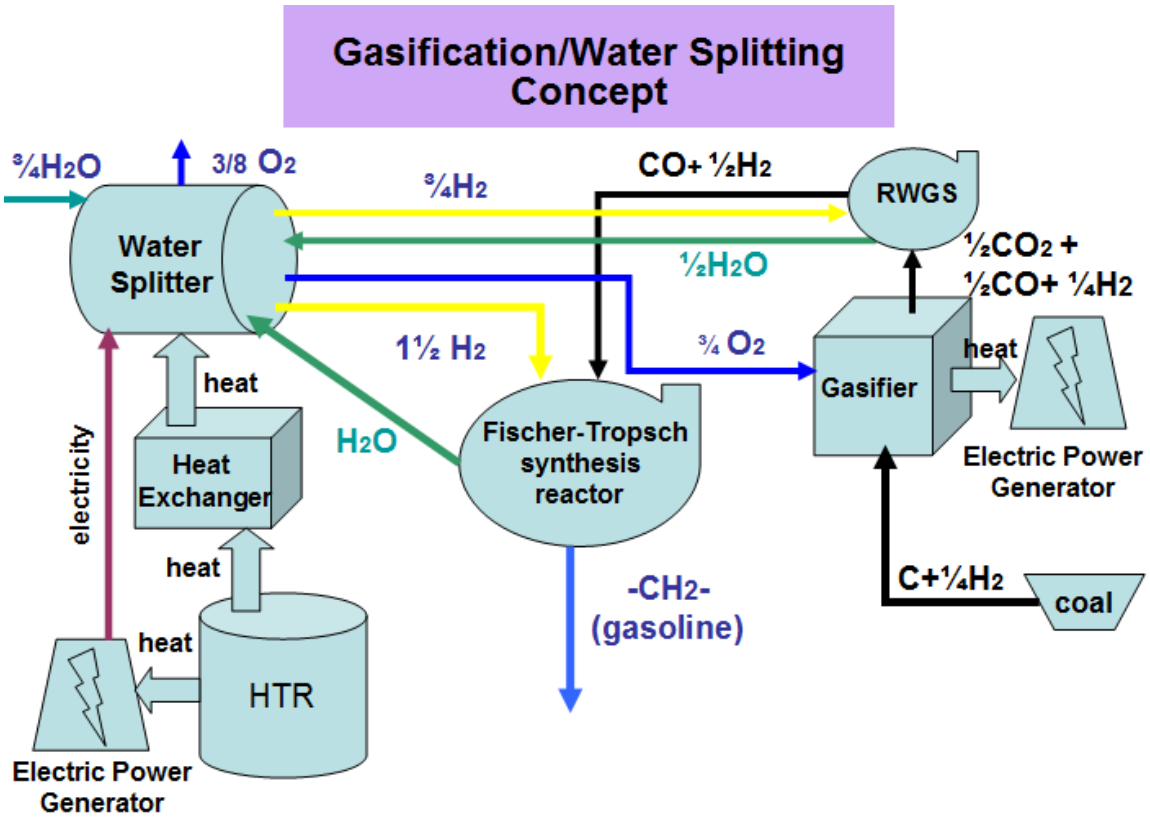

Fig. 3. Cogeneration Synfuel Factory Using Hydrogen from Nuclear Assisted Water Splitting

Advantages:

- Increased process efficiency
- Effective use of coal – conversion to expensive fuel instead of combustion
- Limited temperature requirements on nuclear heat source (T <600oC)

- Possible use of various nuclear reactors (Generation IV):
  - High Temperature Gas Cooled Reactors
  - Lead Cooled Fast Reactor
  - Supercritical Water Reactor
- In optimistic case possible use of Light Water Reactors

Disadvantages:

- Significant challenges for the development of:
  - Dedicated coal system with heat exchangers
  - Dedicated nuclear reactors with heat exchangers
- Safety requirements on tight coupling – unit separations and heat transport on the required distances
- Substantial development required on water splitting process and materials of appropriate properties

Tightly coupled system without water splitting

It is integrated on the process level as much as possible in order to explore synergy effects. It is characterised by the following features:

- Hydrogen is produced form methane reforming/pyrolysis and water gas shift reaction
- It applies gasification plant with suppressed CO2 production or recycle that uses steam from nuclear reactor steam generator
- Boudouard reaction (C+CO2 -> 2CO) drives the process with the heat supplied from HTR

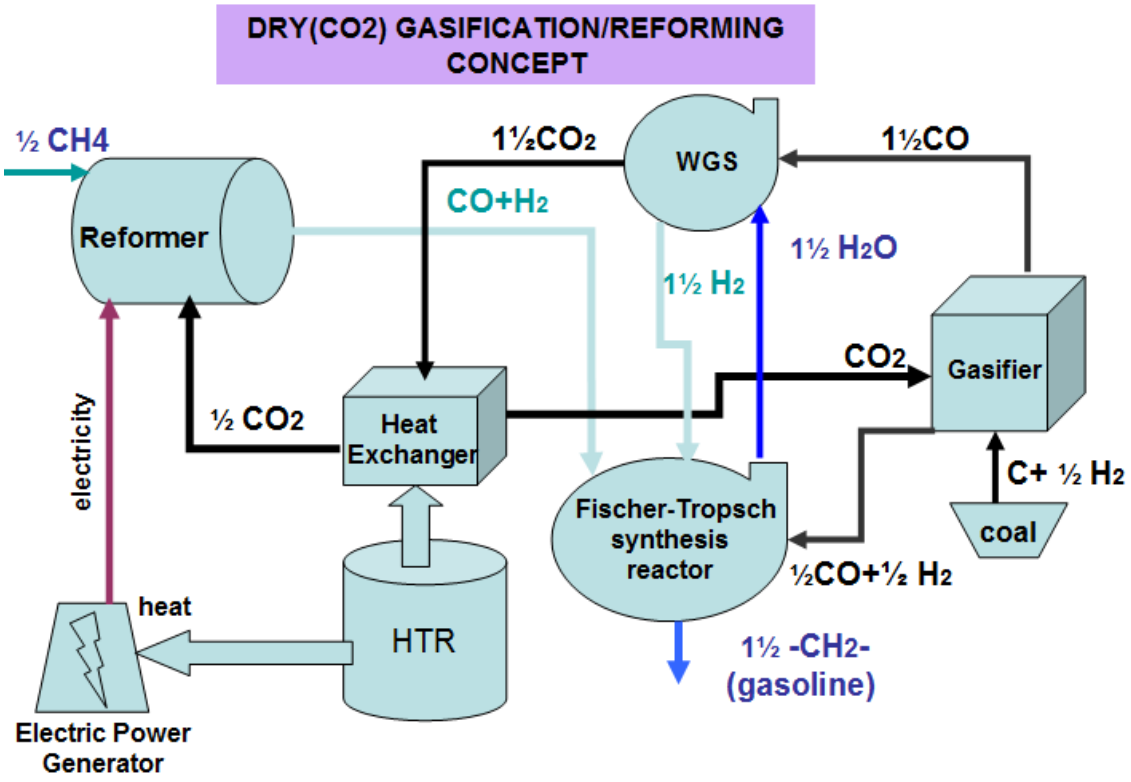

Fig. 4. Cogeneration Synfuel Factory Using Hydrogen from Nuclear Assisted Methane Reforming

Advantages:

- Challenging water splitting is dropped
- Compatibility with the development of cogeneration of heat and power system (CHT) – in order to minimise nuclear system (HTR) customisation
- Effective use of coal – conversion to expensive fuel instead of combustion
- Relaxed safety requirements on tight coupling – no hydrogen or oxygen process coupled to nuclear one

Disadvantages are :

- Significant challenges or new R&D areas :
  - Dedicated coal system with heat exchangers
  - R&D needed on IHX adjustment to CO2 as working fluid
  - Dedicated nuclear reactors with heat exchangers
  - Additional R&D needs on catalysis for Boudouard reaction

5 HYDROGEN PRODUCTION OPTIONS FOR NCTL

Hydrogen is already a significant chemical product. Current world production is not precisely monitored, but is estimated at around 45 million tons, or 500 million Nm3, per year. Ammonia and methanol production is by far the largest consumer of hydrogen, accounting for 58% of global consumption. Petroleum refineries accounted for the next 37%, and 5% was used in other applications, like: hydrogenation of processed foods, thermal treatment of metal components, production of glass or semiconductors, space propulsion etc. It is commonly expected that in near future hydrogen will play important role as an environmentally friendly energy carrier. Finally, the perspectives of all coal-to-liquid technologies depend on the progress in new, emissions-free hydrogen production methods.
Hydrogen can be produced from different feedstocks, by variety of processes:

- natural gas
- steam methane reforming
- partial oxidation
- autothermal reforming
- thermal decomposition of methane
- liquid hydrocarbons
- partial oxidation
- coal
- various gasification processes
- biomass
- various gasification processes
- water
- alkaline electrolysis
- polymer electrolyte membrane (PEM) electrolysis
- high temperature electrolysis
- thermo-chemical water splitting
- photo-electrolysis (photolysis)
- photo-biological production (biophotolysis)

The first commercial production technology, dates from the late 1920s, was the electrolysis of water for pure hydrogen production. In the 1960s, the industrial production of hydrogen shifted slowly towards a fossil-based feedstock, which is the main source for hydrogen today. At present, about 96% of hydrogen is made from fossil fuels: 48% from natural gas, 30% from liquid hydrocarbons and 18% from coal. Unfortunately, this gives rise to huge carbon dioxide emissions: depending on the feedstock, each tonne H2 produced gives rise to 7-11 tonnes of CO2. Electrolysis accounts for only 4%.

Natural gas is an important resource for near-term hydrogen production – it has a high hydrogen-to-carbon ratio so it emits less CO2 compared to other hydrocarbons. It offers also the lowest production costs comparing to other feedstocks. Due to concerns about a limited supply the natural gas is not considered a long-term option, but recent developments of shell gas technology as well as discoveries of huge shell gas fields may change this point of view.

Coal is an attractive feedstock due to its natural abundance and low, traditionally stable prices. Coal gasification is an established technology used in hydrogen production today, but additional technical and economic considerations for capture and storage of CO2 will be necessary. Due to the lower ratio of hydrogen to carbon, which in natural gas is 4:1 and in carbon is 0.8:1.8, the hydrogen produced from coal is almost twice as expensive as from natural gas. Higher are also emissions of CO2 and other pollutants such as SO2 and CO.

Biomass feedstocks are unrefined products with inconsistent quality and poor quality control. The production methods vary according to crop type, location and climatic variations. But, being the renewable feedstock, it is considered as attractive due to favourable CO2 balance.

Water would be the most desirable source of hydrogen, virtually unlimited and almost equally distributed all over the world. Providing non-combustion energy source it also would allow for emission-free hydrogen production. Unfortunately, at present the costs are significantly higher than for other feedstocks [29].

Steam Methane Reforming (SMR)

Steam methane reforming is a process to produce hydrogen, which consists of the following three steps:

- **reformation of natural gas** - involves methane reacting with steam to produce a synthesis gas (syngas), being a mixture of H_2 and CO. The reforming step, described by the following reaction:

  $$CH_4 + H_2O \rightarrow 2H_2 + CO \qquad \Delta H = +206\ kJ/mol$$

  is carried out in a reformer containing tubes filled with nickel catalyst at temperatures between 500ºC and 950ºC and a pressure around 3 MPa. An excess of steam is used to enhance conversion and to prevent thermal cracking and coking via the nickel-catalyzed Boudouard reaction [30]:

  $$2CO \rightarrow CO_2 + C \qquad \Delta H = -172\ kJ/mol$$

  This steam excess instead promotes the second step in the process: the conversion of syngas to the H_2 product. Since the first reaction is highly endothermic, the process is allothermal: the required heat is produced outside of the reactor. Usually this heat is produced by burning part of methane (and emitting CO_2), but the emission-free heat source, e.g. nuclear, would allow for significant reduction of CO_2 release;

- **water gas shift reaction (WGS)** - CO produced in the first step reacts with steam over a catalyst to form H_2 and CO_2:

  $$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -41\ kJ/mol$$

  This process occurs in two stages, consisting of a high temperature shift (HTS) at 350ºC and a low temperature shift (LTS) at 190-210ºC;

- **purification** - removes water, methane, CO_2, N_2, and CO, producing 99.99+ pure hydrogen product. After that the process gas may be treated to remove CO_2 if sequestration is desired. Pressure swing adsorption (PSA) is a commonly used industrial process for the purification of gas streams. Pressure swing systems are based on selective adsorbent beds. A gas mixture is introduced to the bed at an elevated pressure and the solid adsorbent selectively removes certain components of the gas mixtures, allowing the unadsorbed components to pass through the bed as purified product gas. Multiple beds are cycled in the process, allowing the adsorbed pollutants to be periodically desorbed.

Another hydrogen separation method is used in membrane reactors, where the gas mixture is passed at high pressure over a heated metal membrane such as palladium or palladium alloys. The membrane reactors are described later.

Steam methane reforming is the most widely used method for hydrogen production in the chemical and petrochemical industries. SMR without CO_2 sequestration is currently the most economic production technique due to the high efficiency of the process and the low cost of supply of natural gas. A disadvantage is that CO_2 capture and sequestration may be necessary in the future, resulting in additional capital and operating costs. Another concern is the long-term supply of methane. For these reasons, SMR is generally projected to be a transition technology for the hydrogen economy, but will most likely be replaced later by other techniques for long term production.

Membrane reactors

In conventional MSR the hydrogen is purified by distillation and pressure-swing adsorption. Membrane reactors would be expected to reduce the operating temperature by the use of hydrogen permselective membranes. A number of studies of membrane reactors for MSR using dense membranes, such as palladium, have been reported. These membranes allow 100% pure hydrogen in the permeate stream, but have important disadvantages, like high cost or degradation by acidic gases and carbon. Alternatively to dense membranes, the other types under investigation are: porous membranes (silica, alumina, carbon), polymeric membranes and ion-conductive membranes. The diagram of the membrane methane reforming is shown in Fig. 5.

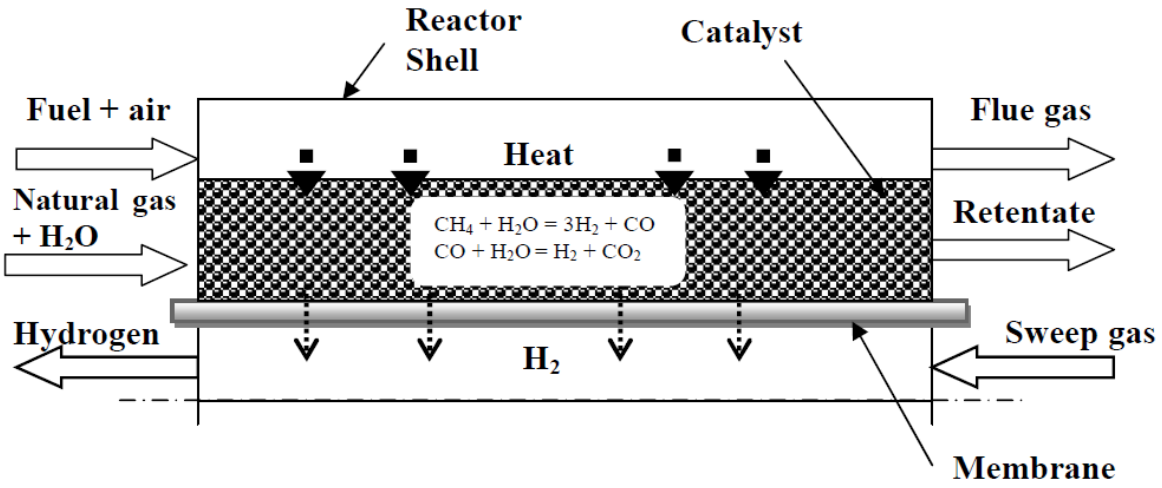

Fig. 5. Diagram of membrane methane reforming

The hydrogen molecule is first adsorbed on to a palladium site, and then is dissociated into hydrogen atoms. These atoms then diffuse through the membrane and eventually recombine to form hydrogen molecules at the back surface of the metal membrane. As long as there are no leaks through or around the membrane, the output hydrogen is 100% pure, since no other gas can pass through a solid metal membrane. However, for effective mass transfer through the membrane, gas pressures far greater than those for the PSA are necessary.

The membrane reactors can be used both in allothermal and autothermal methane reforming systems. This technology is however not mature enough to allow for design of large scale commercial plants, since at present the installations have the hydrogen flow rate about 6 Nm^3/h. There are also still problems with durability, selectivity decrease and production costs. From the other hand, the further progress in research

on membrane reactors would lower the hydrogen production costs and allow for construction of middle-scale local facilities [29,30].

Water electrolysis

Water electrolysis is the process whereby water is split into hydrogen and oxygen through the application of electrical energy, according to equation:

$$H_2O + \text{electricity} \rightarrow H_2 + \tfrac{1}{2}O_2 \qquad \Delta H = 285.8\ kJ/mol$$

The theoretical voltage for this decomposition of water at normal conditions is 1.23 V, and if the cell is allowed to absorb heat from the surroundings, the process efficiency exceeds 100%, but the reaction rates are very slow. In practice, higher voltages are applied, increasing the reaction rates, but decreasing energy efficiency to 50–80%, mainly due to heat losses to the surroundings. The necessary voltage may be lowered by means of catalysts or sophisticated electrode surfaces that increase surface area.

The amount of gases produced per unit time is directly related to the current that passes through the electrochemical cell. At room temperature pure water is a fairly good insulator – unless a very large potential is applied the process would be very slowly limited by the overall conductivity. If a water-soluble electrolyte is added, the conductivity of the water rises considerably. Despite the fact that the discovery of electrolytical water decomposing was first observed in acidic water, in industrial plants the alkaline medium is preferred, because corrosion is more easily controlled and cheaper construction materials can be used compared to acidic electrolysis technology.

Water electrolysis is an established method of hydrogen production, and its theoretical efficiency is quite high. Practically it is much less due to the relatively low efficiencies of electricity production. It is estimated that the electricity costs contribute to 70–90% of the of the final product cost.

Hydrogen produced via electrolysis can result in zero or near-zero greenhouse gas emissions, depending on the source of the electricity used. The emissions resulting from electricity generation must be considered when evaluating the environmental benefits of electrolytic hydrogen production technologies. Due to that, the electrolysis with electricity from nuclear power plants would allow for real emission-free hydrogen production [31].

Alkaline electrolysis

Alkaline electrolysers use an aqueous KOH solution (caustic) as an electrolyte that usually circulates through the electrolytic cells. The following reactions take place inside the alkaline electrolysis cell:

Electrolyte: $4H_2O \rightarrow 4H^+ + 4OH^-$
Cathode: $4H^+ + 4e^- \rightarrow 2H_2$
Anode: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$
Overall: $2H_2O \rightarrow O_2 + 2H_2$

Electrolysis plants with normal or slightly elevated pressure usually operate at electrolyte temperature of 70–90ºC, cell voltage of 1.85–2.05 V and consume 4–5 kWh/m^3 H_2, which is obtained at a purity of 99.8% and more. Pressure electrolysis units run at 0.6–20 MPa without any significant influence on the power consumption, but the higher pressures of delivered hydrogen meet the demands of many consumers, allowing for avoidance of additional compression costs.. Performances of selected commercial alkaline electrolysers are presented in Table 4.

Alkaline electrolyser technology is currently most suitable for large scale commercial production of hydrogen. It may be expected that its efficiency will increase with the development of new materials.

be implemented in another way. That is using methane to produce hydrogen through pyrolysis or steam or carbon dioxide (dry) reforming processes in allothermal version (with an external heat source for the process). Similarly, we should use allothermal coal gasification, which will decrease its oxidation and carbon

Table 4. Comparison of commercial alkaline electrolysers

Manufacturer	Model	Capacity [Nm^3/h]	Max H_2 pressure [MPa]	Energy required [kWh/Nm^3]	Efficiency inc. el. prod. [%]
Hydrogenics	IMET 300 IMET 1000	3 90	2.5 2.5	4.9 4.8	24 24
Teledyne	Titan™ EC Titan™ HM	56 11	0.8 1.0	5.6 5.3	21 22
Norsk Hydro Electrolyser	5040 (4000A) 5040 (5150A) HPE	377 485 65	atm atm 1.2	4.8 4.8 4.8	24 24 24
IHT	Lurgi Bamag	760 330	3.2 atm	4.6 4.5	25 26
Accagen	VHP	100	20.0	6.3	18
Idroenergy		64	0.4	6.0	19

PEM water electrolysis

The Proton Exchange Membrane electrolysis, also referred to as SPE or Solid Polymer Electrolyte electrolysis, is based on the use of a polymeric proton exchange membrane as the solid electrolyte. The membrane allows the H^+ ion to transfer from the anode side of the membrane to the cathode side, where it forms hydrogen. The following reactions are involved:

Anode: $H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$
Cathode: $2H^+ + 2e^- \rightarrow H_2$

The SPE membrane also serves to separate the hydrogen and oxygen gasses, as oxygen is produced. Although the principle of operation is just reverse of fuel cell operation, the materials are different. Due to corrosion on the oxygen side, metallic components and platinum catalysts are used. The standard membrane material used in PEM water electrolysis units is Nafion™ 117 manufactured by DuPont.

The following advantages of PEM over alkaline technology have been considered:

- greater safety and reliability due to absence of KOH electrolyte;
- higher operating pressures (up to several tens MPa) thanks to membrane materials which could sustain high differential pressure without damage;
- membranes were efficient in preventing gas mixing;
- more compact design, as the cells can be operated up to several A/cm^2 with typical thickness of a few mm;
- higher turn-down ratio.

The main drawback of this technology is the limited lifetime of the membranes as well as high costs (10^3 – 10^4 \$/kW vs $<10^3$ \$/kW for alkaline electrolysers). At present there are a few PEM electrolyser manufacturers. Selected technical data are shown in Table 5.

Table 5. Comparison of commercial PEM electrolysers

Manufacturer	Model	Capacity [Nm^3/h]	Max H_2 pressure [MPa]	Energy required [kWh/Nm^3]	Efficiency inc. el. prod. [%]
Proton	HOGEN H HOGEN 380	6 10	1.5 1.4	6.3 6.3	18 18
Qualean	QL-17000 QL-85000	1 5	2.0 2.0	7.5 5.8	15 20

With relatively high cost, low capacity, lower efficiency and short lifetimes, the PEM electrolysers currently available are not as mature as alkaline electrolysers. It is expected that the performance of PEM electrolysers can be improved significantly by additional work in materials development and cell stack design [32].

High temperature electrolysis

High temperature electrolysis, also referred to as steam electrolysis or solid oxide electrolysis, is a technology that reaches higher total energy efficiency compared to alkaline and PEM electrolysis. Despite the fact that the total energy needed for the electrochemical decomposition of water decreases only slightly with increasing temperature, the required electrical energy decreases considerably. Therefore an increasing amount of the total energy could be supplied as heat, which is much cheaper than electric energy. In addition, the high temperature accelerates the reaction kinetics, reducing the energy loss due to electrode polarization, thus increasing the overall system efficiency.. At temperatures 800–900ºC the electric power consumption is approximately only 3 kWh/Nm^3 of hydrogen. Typical high temperature device such as the German HOT ELLY system (the late 1970s) achieves 92% electrical efficiency while low temperature electrolysers can reach at most 85% efficiency.

A typical technology applied is the solid oxide electrolyser cell (SOEC), based on the solid oxide fuel cell (SOFC), which normally operates at 700–1000°C. At these temperatures, the electrode reactions are more reversible, and the fuel cell reaction can more easily be reversed to an electrolysis reaction. The high temperature systems use as the electrolyte either oxygen-ion or proton conducting ceramics.

The electrochemical reactions in the O^{2-} conducting SOEC describe the following equations:

Anode: $O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$
Cathode: $H_2O + 2e^- \rightarrow H_2 + O^{2-}$
Overall : $H_2O \rightarrow H_2 + \frac{1}{2}O_2$

The most common cells of this type use yttria or scandia-stabilized ZrO_2 electrolytes that are rapid oxygen conductors and operate at temperatures 800–1000°C. Over the last decade there has been significant R&D to reduce the operating temperature of solid oxide fuel cells to the range 600–800°C. The new electrolytes under investigation are mainly the ones based on CeO_2, $LaGaO_3$ and Bi_2O_3.

The proton conducting electrolytes are based on reactions described by the following equations:

Anode: $H_2O \rightarrow 2H+ + \frac{1}{2}O_2 + 2e^-$
Cathode: $2H^+ + 2e^- \rightarrow H_2$
Overall: $H_2O \rightarrow H_2 + \frac{1}{2}O_2$

The operating temperatures are lower than for the oxygen-ion conducting electrolytes. For often reported $BaZrO_3$ electrolyte it is 500–800°C, but some more complex materials were successfully operated at 460–600°C.

It must be noted that this technology is still in the development stage and the main R&D needs relate to materials which can stable operate at high temperatures. At present, despite this high efficiency with respect to electricity, the high temperature system still produces hydrogen at about four times the cost of the steam reformed hydrogen [33,34].

Thermochemical water splitting

Thermochemical water splitting is the conversion of water into hydrogen and oxygen by a series of thermally driven chemical reactions. There are more than 200 thermochemical cycles that have been studied for the past 35 years, but the technical status of many of them is at the experimental stage [35,36]. Only a small part of these cycles has been identified as promising for hydrogen production. Usually, the most important limiting factor is the highest reaction temperature required. In the case of so called Solar Thermo-Chemical Water Splitting Cycles the solar source of heat allows even for temperatures exceeding 1000°C. If the process heat is to be delivered by the high temperature nuclear reactors (HTR), even the temperature 850°C is considered as to high. Beside the peak temperature another key issues usually are:

- number and complexity of reactions involved
- multiphase or competing chemical reactions
- aggressive or toxic reagents
- durability of materials at high temperatures
- cost of materials or reagents
- process efficiency
- economics of scaling
- pollutions in not fully closed cycles

Taking all these parameters into account, only a few low temperature thermochemical water splitting cycles have been identified as promising. These are collected in the Table 6.

Table 6. Most promising low temperature thermo-chemical cycles

Cycle	Peak Temp. [°C]	Energy Efficiency [%]	Advantages	Key issues
Sulphur Iodine	850	30-50	+ High efficiency + No electrolysis + International R&D	- High temperature - HI distillation - Highly aggressive acids - Iodine hazard and cost
Hybrid Sulphur	at least 850	40-50	+ High efficiency + No halogens + Least complex S cycle	- High temperature - Electrolysis efficiency - Economic scaling
Hybrid S-Br	at least 850	40	+ Cont. 1.5 year demo + No major instabilities	- High temperature - Electrolysis efficiency - Economic scaling - Bromine hazard and cost
UT-3 (Ca-Br)	750	40-50	+ High efficiency	- Durability of solid chem. - Gas-solid reactions
Hybrid Cu-Cl	550	40-50	+ Lowest peak temp.	- Electrolysis efficiency - 3-phase reaction
Iron Chlorine	650	40-50	+ Low peak temperature	- Competing reactions
Hybrid Cu-S	830	70	+ Highest efficiency	- High temperature - Economic scaling
Vanadium Chlorine	925	40-50	+ Improvement possible	- Very high temperature - O_2 membrane

From this list three cycles are considered the leading candidates for future implementation: Sulphur-Iodine (SI or IS), Hybrid Sulphur (HyS) and Hybrid Cu-Cl. These cycles are described in details.

Sulphur-Iodine Cycle (SI)

The SI cycle was invented by General Atomics in the 1970s. This process is based on the decomposition of two acids at high temperature: sulphuric acid (H_2SO_4), yielding O_2 and SO_2, and hydriodic acid (HI), yielding H_2 and I_2. These two acids are subsequently reconstituted in Bunsen reaction. Although the SI cycle is regarded as 3-step cycle, in fact it comprises four reactions:

① $H_2SO_4 \rightarrow H_2O + SO_3$ (400–600°C)

$SO_3 \rightarrow SO_2 + \frac{1}{2}O_2$ (800-900°C)

② $2HI \rightarrow H_2 + I_2$ (200–400°C)

③ $SO_2 + 2H_2O + I_2 \rightarrow H_2SO_{4\,(aq)} + 2HI_{(aq)}$ (25–120°C)

In the second step iodine (as well as remaining water and SO_2) are separated from hydrogen by condensation. Then, in the third step (Bunsen reaction) HI must be effectively separated – usually by distillation – as this reaction is reversible. The ongoing R&D concentrates on the optimal distillation scheme, but also membrane separation is under investigation.

The SI cycle involves only gas and liquid processes, therefore is well suited for continuous operation. It is completely closed, allowing for operation without any effluents. With an efficiency of around 50% it is also more efficient than electrolysis. From the other hand, the peak temperature is too high for the nuclear heat applications. Another key issue are corrosive reagents used at high temperatures, therefore the selection of materials with sufficient corrosion resistance under the process conditions is of key importance to the economic viability of this process.

At present most R&D effort in thermo-chemical cycles concentrates on SI cycle. This process, currently under investigation in USA, Europe, Japan and Korea, has been indicated (along with the HyS cycle) as the leading candidate for future implementation [37].

Hybrid Sulphur Cycle (HyS)

The HyS cycle, also referred to as the Westinghouse Hybrid Cycle, was invented by Westinghouse in the 1970s. It substitutes the iodine involving reactions of SI cycle by SO_2 electrolysis:

① $H_2SO_4 \rightarrow H_2O + SO_3$ (400–600°C)

$SO_3 \rightarrow SO_2 + \frac{1}{2}O_2$ (800-900°C)

② $SO_2 + 2H_2O \rightarrow H_2SO_4 + H_2$ (20–110°C U=0.17V)

The last reaction runs under pressure 0.2–1 MPa. The presence of SO_2 along with water in the electrolyser reduces the required electrode potential well below 1.23V required for pure water electrolysis. The theoretical potential required for electrolysis with SO_2 is only 0.17V, therefore the total energy required at the electrolyser can be significantly reduced.

The HyS cycle involves less reactions than SI cycle and requires only one intermediate element which is quite cheap. No toxic halogens are used. Like in the SI cycle, all reagents are either in gas or in liquid phase. On the other hand, this cycle does require electric energy, which decreases total efficiency (~47%) and may complicate process scaling. The peak temperature is the same as in SI cycle – too high for the nuclear heat applications. Moreover, the electrolysis conducted in strong acid medium leads to serious corrosion issues.

Nevertheless, the HyS process has been granted the highest score in evaluation prepared by General Atomics [38].

Hybrid Copper-Chlorine Cycle (Cu-Cl)

This cycle, being developed mainly in Canada, attracts significant attention since its peak temperature is only 550°C. At this temperature, the process heat could be easily delivered by high temperature nuclear reactors. There are two versions of process: original 5-step version, presented below, and modified 4-step version.

① $2Cu_{(s)} + 2HCl_{(g)} \rightarrow 2CuCl_{(l)} + H_{2(g)}$ (430-475°C)

② $4CuCl_{(s)} \rightarrow 4CuCl_{(aq)} \rightarrow 2CuCl_{2(aq)} + 2Cu_{(s)}$ (ambient U=0.65V)

③ $2CuCl_{2(aq)} \rightarrow 2CuCl_{2(s)}$ (<100°C)

④ $2CuCl_{2(s)} + H_2O_{(g)} \rightarrow CuO*CuCl_{2(s)} + 2HCl_{(g)}$ (350–400°C)

⑤ $CuO*CuCl_{2(s)} \rightarrow 2CuCl_{(l)} + \frac{1}{2}O_{2(g)}$ (530°C)

In the second version first two reactions are coupled together:

①② $2CuCl_{(aq)} + 2HCl_{(aq)} \rightarrow 2CuCl2_{(aq)} + H_{2(g)}$ (80°C U=0.65V)

Hydrogen is produced in the step ①, but – depending on particular version – it is either thermochemical or electrochemical process. The potential required for electrolysis is as low as 0.5V, but 0.65V is used to achieve better current density.
Drying (step ③) is the most energy intensive step in the whole process. Although the amount of heat required is much higher than for other steps, it occurs at a relatively low temperature and therefore can be obtained from low-grade waste heat improving the cycle efficiency.
The highest temperature in the whole cycle is required for oxygen production (step ⑤) where the solid copper oxychloride at 530ºC produces gaseous O_2 and liquid CuCl. Practically the oxygen contains some impurities: Cl_2, CuCl vapour and trace amounts of HCl and water vapour. The molten CuCl may contain some amounts of solid $CuCl_2$, remaining after incomplete decomposition in step ④.

The Cu-Cl cycle offers the lowest peak temperature, suitable for nuclear heat source. Moreover, it is able to utilize low-grade waste heat to improve energy efficiency. From the other hand, the most challenging issues are:
- multiphase reactions (3-phase);
- corrosive working fluids;
- solids handling between processes;
- separation of impurities;
- lack of accurate thermochemical data for the copper chlorides.

Research recently done by AECL has shown, that the 4-step cycle is more promising than intermediate production of copper in the 5-step cycle. The efficiency of electrolysis step is likely to be improved by application of proton-conducting polymer electrolyte membranes (PEM) as well as better electrode materials. Additional gains are expected from better waste heat utilization. Recent analyses presented by Aspen Plus show that the total efficiency of the cycle may be as good as 55% at 550ºC.

The Cu-Cl cycle was identified by Atomic Energy of Canada Limited (AECL), as the most promising cycle for thermochemical hydrogen production with the Generation IV nuclear reactor SCWR [39,40,41].

Summary of hydrogen production methods

A comparison of the presented hydrogen production methods is provided in the Table 7. Currently only the methane and coal based technologies are used for the large scale hydrogen production. Only 4% of hydrogen come from the low temperature electrolysis. The comparison of hydrogen prices is difficult since there is strong dependency on the feedstock as well as the electricity cost. Simultaneously, the hydrocarbon based technologies emit huge amounts of CO_2 but, at present, this fact is not reflected in the hydrogen price. Another difficulty arises from the comparison of technologies working in different scales. It should be also observed, that the price depends also on such parameters as the required purity or pressure. Finally, many of presented technologies are currently under intensive R&D and the price estimations may be inaccurate.

Table 7. Summary of hydrogen production technologies

Production Technique	Efficiency [%]	Estimated price [$/kg$H_2$]	Scale	Status	Major Advantages	Major Disadvantages
Steam Methane Reforming	83	1.4 – 4.0	large	mature	- High efficiency - Proven technology - Economically justified	- Emission issues - Limited long-term natural gas supply
Membrane Methane Reforming	70 – 80	no data	small	R&D	- Lower temperatures - Easier gas separation	- Emission issues - Membrane costs - Small scale
Low Temperature Electrolysis	25	3.7 – 6.5	small	available R&D required	- Proven technology - Excellent feedstock - No emissions	- Low efficiency - Expensive
High Temperature Electrolysis	30	3.7 – 6.5	small	R&D	- Excellent feedstock - No emissions - Better efficiency	- Low efficiency - Material issues
SI cycle	30 – 50	2.0 – 8.0	small	R&D	- Excellent feedstock - No emissions	- High temperature - Aggressive reagents - Material issues
HyS cycle	40 – 50	2.0 – 8.0	small	R&D	- Excellent feedstock - No emissions	- High temperature - Aggressive reagents - Material issues
Cu-Cl cycle	40 – 50	1.5– 8.5	small	R&D	- Excellent feedstock - Reasonable temp. - No emissions	- 3-phase reactions - Aggressive reagents - Material issues

The most important technological parameters of presented methods are collected in the Table 8. In case of methods based on natural gas or coal, the energies shown do not include expenditure for CO2 sequestration. From the other hand, the electric energy is produced with efficiency ~33%, and due to that the real energy required in electrochemical processes is higher than the one shown in the table.

Table 8. Basic technical data of hydrogen production technologies

Production Technique	Thermal energy [MJ/kgH_2]	Electrical energy [kWh/kgH_2]	Total energy [MJ/kgH_2]	Temperature [°C]	Pressure [MPa]
Steam Methane Reforming	170	–	170	850 - 900	0.2 - 0.3
Membrane Methane Reforming	150	–	150	400 - 600	0.2 - 2.5
Low Temperature Electrolysis	–	56	102	80 - 100	at. - 2.5
High Temperature Electrolysis	85	38	154	800 - 850	0.2 - 0.6
SI cycle	284	–	284	750 - 850	0.2 - 0.4
HyS cycle	119	43	274	750 - 850	0.2 - 0.4
Cu–Cl cycle	140	17	171	450 - 550	atm.

6 CONCLUSIONS

The use of heat from a high-temperature nuclear reactor for thermo-chemical processing of coal will substitute the presently used burning with flameless processes. That will result in an economical use of the raw material and radical reduction in the emissions of CO2 and other harmful gases. Developing this method would also bring other, non-the-less-important, long-term and strategic advantages. These consist in changing the technological profile of the fuel and energy sector, making it a flexible and diversified system, which would guarantee a much higher level of strategic safety, but also be ready to enter the era of hydrogen fuel in the future. In such a system new opportunities are open, connected with processing of natural gas, or, reversely, producing its substitute. Introducing the solution postulated here will make it possible to implement and further develop the nuclear reactors technology of the highest generation in Poland, in a way that would be blended in with traditional energy technologies, alleviating the existing social resistance in this area. Synergetic combining of coal and nuclear power industries will have multiple positive consequences for the whole energy sector and the economy as a whole.

Poland, due to its leading position in coal exploitation and the lack of significant resources of liquid fuels is predestined for introducing the discussed technology in Europe. On the other hand, the lack of energy producing nuclear reactors based on the second and third generation technology can even be seen as an advantage. That is because the high-temperature reactors, based on different technologies are not complementary but rather competitive for the existing technologies. Besides, maintaining different types of reactors in one country involves doubling a lot of work, legal regulations etc. Introducing new type reactors in Poland would then be possible without a potential conflict of interests with the existing technology. Certainly, a problem to overcome is re-creating and developing the scientific and technological staff necessary to implement the fourth generation reactors. Such a task will require significant investment – first of all from the state – in education and scientific research. Such investment is strongly desired, as they will provide for the modernization of the economy towards the most modern and technologies.

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