Production of Hydrogen

An analysis of research activity based on a review of patent literature

November 2021 – Gilbert Voortmans

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Executive Summary

Climate change presents one of the biggest challenges of our times according to the European Environment Agency. Keeping the global warming target of 1.5ºC as agreed to in the Paris climate deal is challenging and will require significantly reducing the emission of greenhouse gasses. The renewed interest in hydrogen comes in response to its potential as a climate-friendly energy carrier or feedstock in many applications and sectors.

This report analyzes the patent literature on hydrogen production. Hydrogen can be produced in several ways. Currently, H_2 is mainly produced from methane by the "steam methane reforming" (SMR) process. Other production methods are electrolysis, fermentation, high-temperature water splitting, photobiological water splitting or photoelectrochemical water splitting. Accordingly, sources for hydrogen include fossil fuels and gas as well as renewable resources. The report includes an overall analysis of the patent landscape in the field of hydrogen production as well some more targeted analysis for fossil-based and renewable-based hydrogen. Additionally, developments with respect to hydrogen production using biological processes, photolytic and thermochemical water splitting are reviewed.

The overall analysis shows that the research activity on hydrogen production has been increasing in the last twenty years. Most of the activity is related to climate friendly production of hydrogen with a significantly higher activity on renewable-based hydrogen since 2005. China, US and Japan form the top 3 of countries filing patents. Despite China leading in the number of patent filings, it does not figure in the value analysis of patents.

The analysis of the patents on hydrogen production from non-renewable resources shows that important activity in this field is going towards reducing or eliminating carbon dioxide emissions. Comparing the top 10 list of company and academic institutions for hydrogen production from non-renewable versus renewable resources, it can be concluded that the research on hydrogen production from renewable resources is lead by different players. Striking is that the top 10 of academic institutions for hydrogen production from renewable resources is completely Chinese.

Patent value analysis shows that patents relating to the production of hydrogen using solar energy and from waste or biomass are amongst the patents that have the highest value score in the production of hydrogen from renewable resources. Amongst the use of solar energy, photolytic splitting of water appears to be upcoming. The thermochemical water splitting has a link towards the use of nuclear energy. Finally, about 350 patents are related to biological processes using micro-organisms, algae and fungi to produce hydrogen. The value score of the patents in this field is somewhat less than for the other means of producing hydrogen.

1. Introduction

Climate change presents one of the biggest challenges of our times according to the European Environment Agency[1]. The harmful effects of climate change can already be noted: temperatures are rising, drought and wild fires are starting to occur more frequently, storms are getting more violent, rainfall patterns are shifting, glaciers and snow are melting and the global mean sea level is rising. The flooding in the southern part of Belgium and in parts of Germany in July of this year presents a wakeup call. The global warming is caused by the emission of greenhouse gases of which carbon dioxide (CO_2) and methane represent more than 90%[2].

In Flanders, the chemical industry, refinery and steel industry (basic industries) represent about 80% of industrial emissions of carbon dioxide that is captured by the European carbon dioxide emission trade. To make the basic industries climate neutral by 2050, there are four main themes that are being explored[3]:

1. Use of biomass
2. Circularity (of plastics)
3. Electrification and use of hydrogen
4. Carbon Capture and Storage (CCS) and reuse (CCU)

In a technology report earlier this year, an analysis of the innovative activities in the field of carbon capture and storage was carried out based on the patent literature[4]. The present report provides a similar analysis in respect of the production of hydrogen. Hydrogen is a high-quality energy carrier having a higher energy density per mass than any other fuel and it can be produced in a wide variety of different ways including the use of renewable energy resources. Accordingly, hydrogen will play an important role in decarbonizing energy intensive industries and where end-use electrification is hard to reach through the grid or batteries.[5]

Hydrogen can be produced in several ways including the reforming of natural gas or liquid fuels, electrolysis, fermentation, high-temperature water splitting, photobiological water

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[1] https://www.eea.europa.eu/themes/climate/climate-change-is-one-of (visited June 11th, 2021)
[2] Olivier, J. G. J.; Peters, J. A. H. W. (2019). Trends in global CO_2 and total greenhouse gas emissions. The Hague: PBL Netherlands Environmental Assessment Agency.
[3] Naar een koolstofcirculaire en CO_2-arme Vlaamse industrie, Studie in opdracht van het Agentschap Innoveren & Ondernemen (VLAIO), november 2020. Studie uitgevoerd door Deloitte België in samenwerking met VUB-IES, Climact en AMS
[4] Technology watch - June 2021: Carbon Capture & Storage https://www.essenscia.be/prioriteiten/innovatie/octrooicel/
[5] Prem Kumar Seelam et al. (2020), "Overview on recent developments on hydrogen energy: Production, catalysis, and sustainability", retrieved from https://www.sciencedirect.com/science/article/pii/B9780128171103000011?via%3Dihub

splitting or photoelectrochemical water splitting.[6] Currently, hydrogen is mostly produced on the basis of fossil fuels, in particular natural gas[7].

This report will analyze the patent literature on hydrogen production. Using "Patent Inspiration"[8] various datasets were created as set out in the next section on search strategy and datasets. For these datasets various analysis were carried including activity over time, main players, text pattern analysis enabling insight in the nature of the activity as well as a patent value analysis for providing an indication of key innovations in the respective data sets.

2. Search strategy and datasets

To explore the patent landscape of hydrogen production, a number of different datasets were created. Firstly, a large dataset was created by a search for "hydrogen" appearing within one word of "prepare", "produce" or "manufacture" in the title, abstract or claims, with stemming enabled. However, this resulted also in patents that relate to hydrogenation or production of hydrogen compounds such as hydrogen chloride. These were removed from the results by subtracting patents from the results that have "hydrogenat*" in the title, abstract or claims as well as those that have the terms "hydrogen peroxide", "hydrogen chloride", "hydrogen sulfide", "hydrogen halide", "hydrogen cyanide", "hydrogen bromide", "hydrogen iodide", "hydrogen sulphide" in the title, abstract or main claims. Finally, patents with one of the following CPC classification codes were removed as well as it was found that these were largely irrelevant with respect to the topic: Y02E60/50, C01B15/023, C01B2203/066, C22C1/00, H01M2008/1095, H01M2250/20, H01M8/06, H01M2008/1293,H01M16/003,H01M80625 and H01M8/00. Most of these classifications relate to fuel cells and are therefore more related to the conversion of hydrogen into electricity. Finally, through a further screening of the results a further number of falls hits was removed. The final large dataset contained about 11000 patents and was used to create a general overview of the patent landscape on hydrogen production.

More focussed datasets were created by further narrowing the results of the large dataset. In order to examine in more detail the production of hydrogen from non-renewable resources, the large dataset was narrowed down by searching for patents that had the terms "reform" or "gasification" (stemming enabled) in the title or abstract. Patents that had the term "bio*" in the title, abstract or claims were excluded to remove patents that relate to

[6] US Department of Energy: Alternative Fuels Data Center retrieved on November 10th, 2021 from https://afdc.energy.gov/fuels/hydrogen_production.html
[7] https://www.energy.gov/eere/fuelcells/hydrogen-resources
[8] https://www.patentinspiration.com/

biogas and biomass based production of hydrogen. The thus resulting set had about 1424 patents.

Production of hydrogen from renewable resources was explored by creating two further datasets as follows. Firstly the large dataset was narrowed by searching for patents that included any of the following terms in the title, abstract or claims: "renewable", "clean", "biomass", "green", "solar", "sun", "wind". This resulted in a set of almost 2000 patents.

A further dataset specifically focussed on biological production of hydrogen was created by narrowing the large dataset to patents that also included any of the following terms in the title, abstract or claims: “algea”, “fungi”, "green bacteria", “microorgansims”, "plankton", "bacteria" or “enzyme”. This gave a set of about 350 patents. The combined total of both sets was 2175 showing that there still was a significant overlap between the datasets. Comparing the totals on production of hydrogen from renewable sources (2175) versus non-renewable sources (1424), it is clear that more of the innovation efforts are going into hydrogen production from renewable resources. A conclusion that will become clearer in the following sections.

Finally, datasets were created to examine the developments relating to high temperature water splitting and photoelectrochemical water splitting to produce hydrogen. For this, the large dataset was narrowed down to patents that had the terms: "thermochem*", "thermo-chem*", "plasma chem*", "plasma-chem*" in the title, abstract or claims, yielding a data set of 134 patents on high temperature water splitting. In a similar way, the search terms: semiconductor and ("solar" or "sun")) or "photolyt*" or "photo-therm*" or "phototherm*" yielded a dataset of 98 patents relating to photoelectrochemical water splitting.

3. General overview on hydrogen production

Using the large dataset a general overview and analysis of the field of hydrogen production was made. Firstly, the patent activity over time was analysed by plotting the number of patents against the year of publication of the patents. Figure 3.1 shows the result.

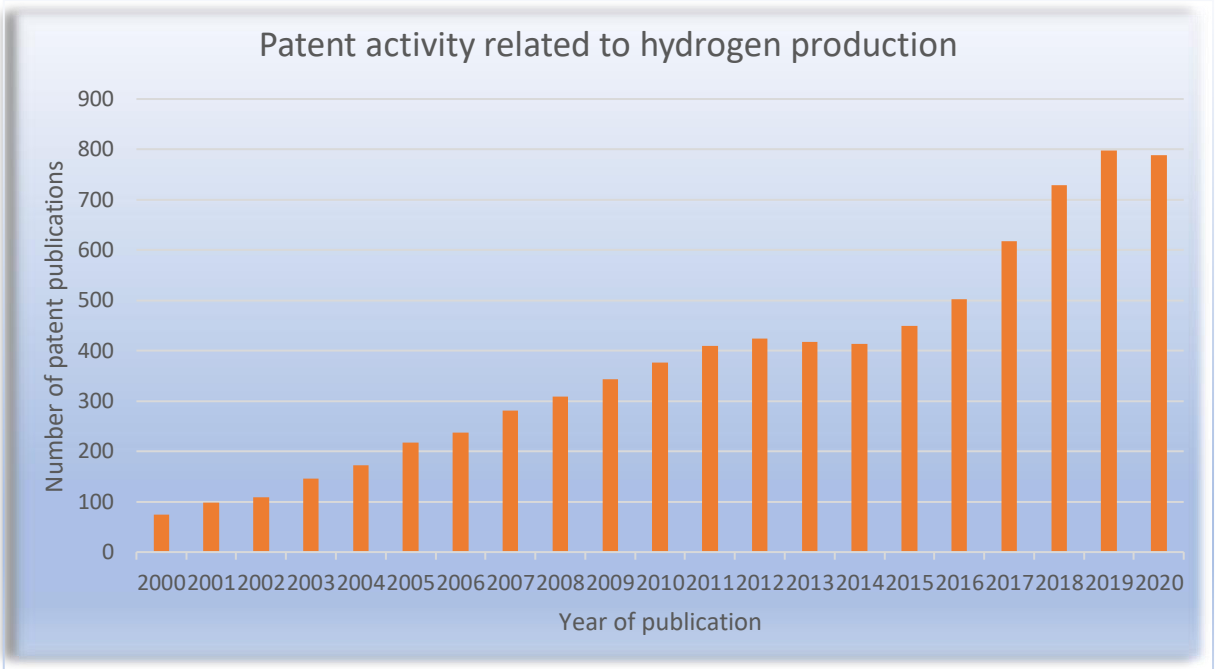


Figure 3.1: patent activity on overall activity on hydrogen production

As can be seen from figure 3.1, there is a clear increasing trend in the number of patent publications relating to production of hydrogen. The trend seems to accelerate in the more recent years. Using text pattern analysis of the claims available in "Patent Inspiration" an attempt was made to compare hydrogen production from renewable resources versus non-renewable resources. The result can be found in figure 3.2. The overall activity profile of the trend for the production of hydrogen is very similar for both types of resources. Both show a peak of activity around 2011-2012. However, the patent activity on production of hydrogen from renewable resources has been increasing more and has been larger than the activity on hydrogen production from non-renewable resource since 2005.

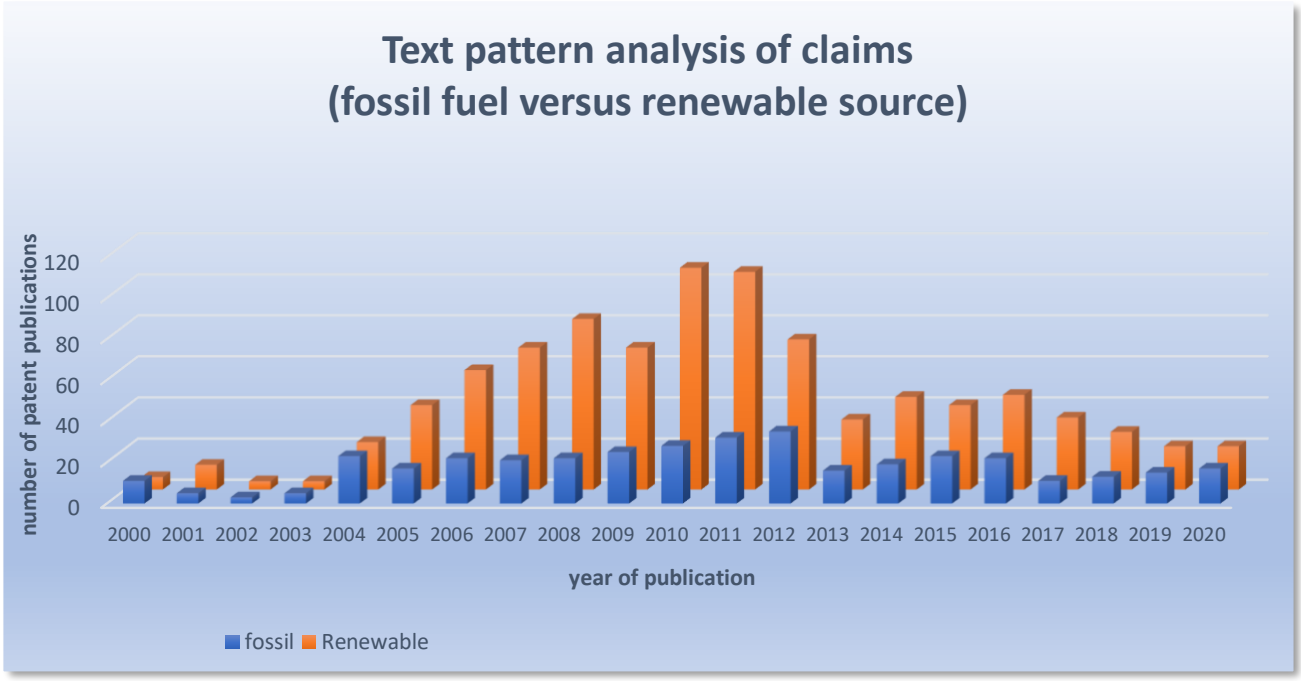


Figure 3.2: comparison of patent activity for hydrogen production from non-renewable (fossil) versus hydrogen production from renewable sources

The dominance of patents on production of hydrogen from renewable resources can also be seen in figure 3.3, which shows the distribution of CPC code classification of patents in the dataset (only the top most occurring classification codes were used to create the figure).

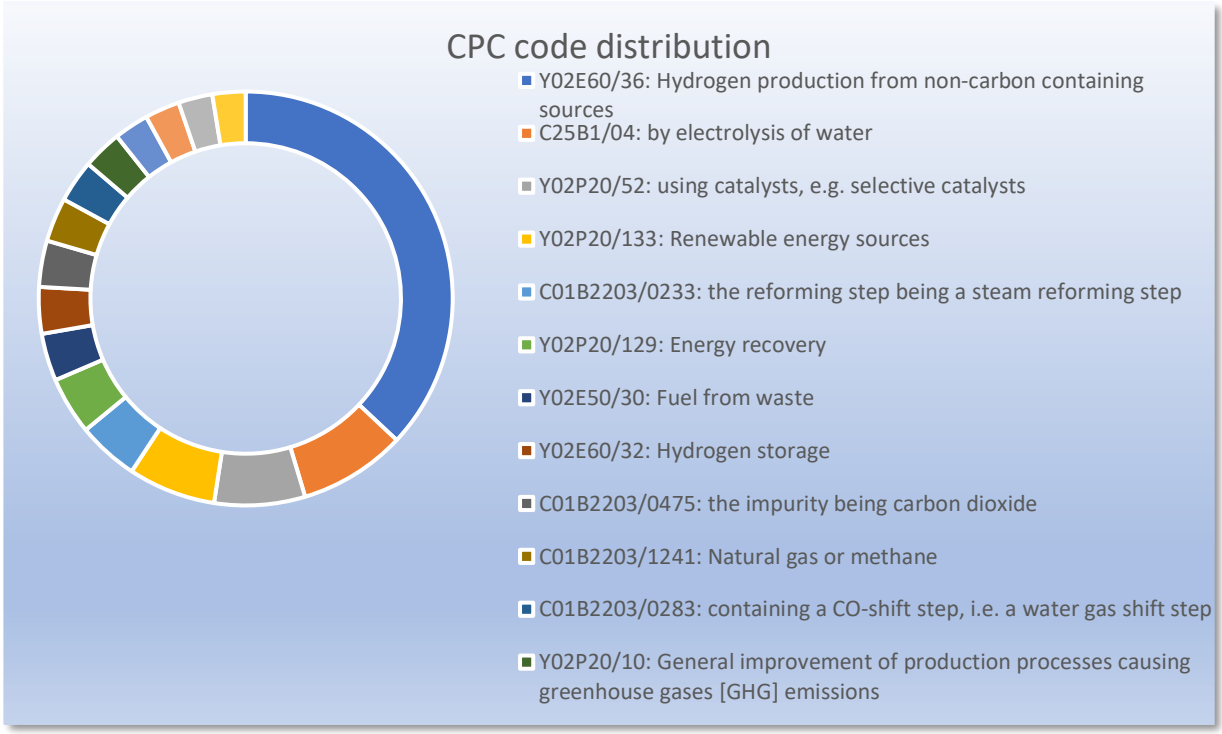


Figure 3.3: CPC classification code distribution for patents on production of hydrogen

The Y02 classification codes, with exception of Y02E60/32 and Y02P20/10, are all codes indicating patents related to hydrogen from renewable resources. They account for significantly more than 50% of the patents. Within the set of patents that relate to production of hydrogen from fossil resources, the codes C01B2203/0475, C01B2203/0283 and Y02P20/10 indicate that within this technology attention is going to capturing CO_2. Reference in this regard is made to the recent technology watch on CCS[9]. Finally, the figure shows that catalysts and of course electrolysis of water play an important role in the production of hydrogen.

Figure 3.4 sets forth the patent activity with time for some countries. There is a clear overall dominance of patents with Chinese inventors. The activity of Japan is noteworthy as well. During 2000 to 2007 they were the most active inventors. Korea is picking up activity in the last couple of years and US is the next active country after China. European inventors lag significantly behind. Only few patents have Belgian inventors and hence are not shown in the figure. However, two interesting patents from the Katholieke Universiteit Leuven of 2015 and 2017 are set forth in table 3.1. These patents relate to production on hydrogen from humidity in air using solar cells. A trial between Fluxys and KU Leuven to further explore the technology was recently announced[10]

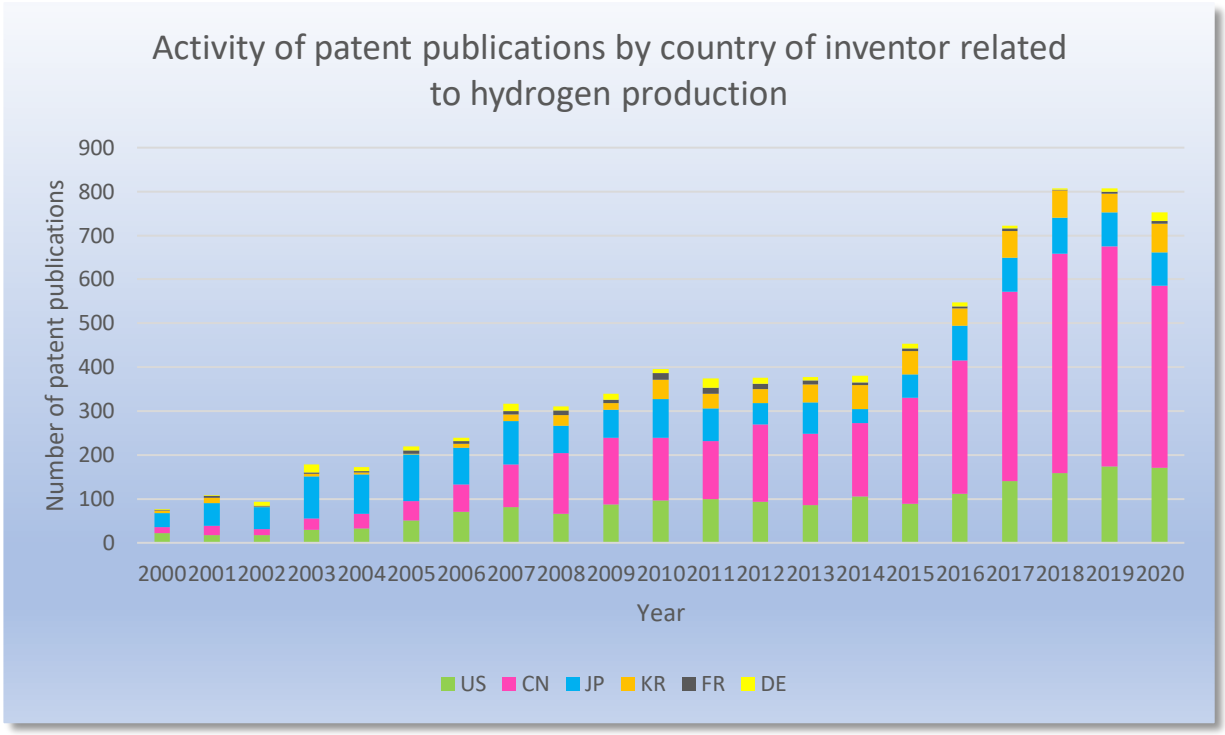


Figure 3.4: patent activity by country of the inventor

[9] Technology watch - June 2021: Carbon Capture & Storage https://www.essenscia.be/prioriteiten/innovatie/octrooicel/

[10] Solar magazine no. 1 (2021) retrieved on November 11th, 2021 from https://solarmagazine.nl/nieuws-zonne-energie/i23650/ku-leuven-en-fluxys-starten-proef-met-look-a-like-zonnepaneel-waterstof-uit-licht-en-lucht

Table 3.1.: Patents with Belgian inventors

Publication number	Publication date	Title	Inventor
WO2017190202A1	09 nov 2017	Hydrogen producing apparatus	BAETS, Roeland,BOSSEREZ, Tom,MARTENS, Johan,RONGÉ, Jan,TROMPOUKIS, Christos
GB2516866A	11 feb 2015	Device for hydrogen and electricity production	JOHAN MARTENS,JAN RONGÉ

Figure 3.5 shows the number of patent publications of the country of the inventor in various CPC classes. In this way, a picture can be drawn of the nature of the activity of the countries. The predominant amount of activity for all countries is in the area of hydrogen production from renewable resources as shown in particular by the activity in Y02E60/36 (production of hydrogen from non-carbon sources). The US shows also significant activity in CPC classes that can be associated with production of hydrogen from non-renewable resources (C01B classes).

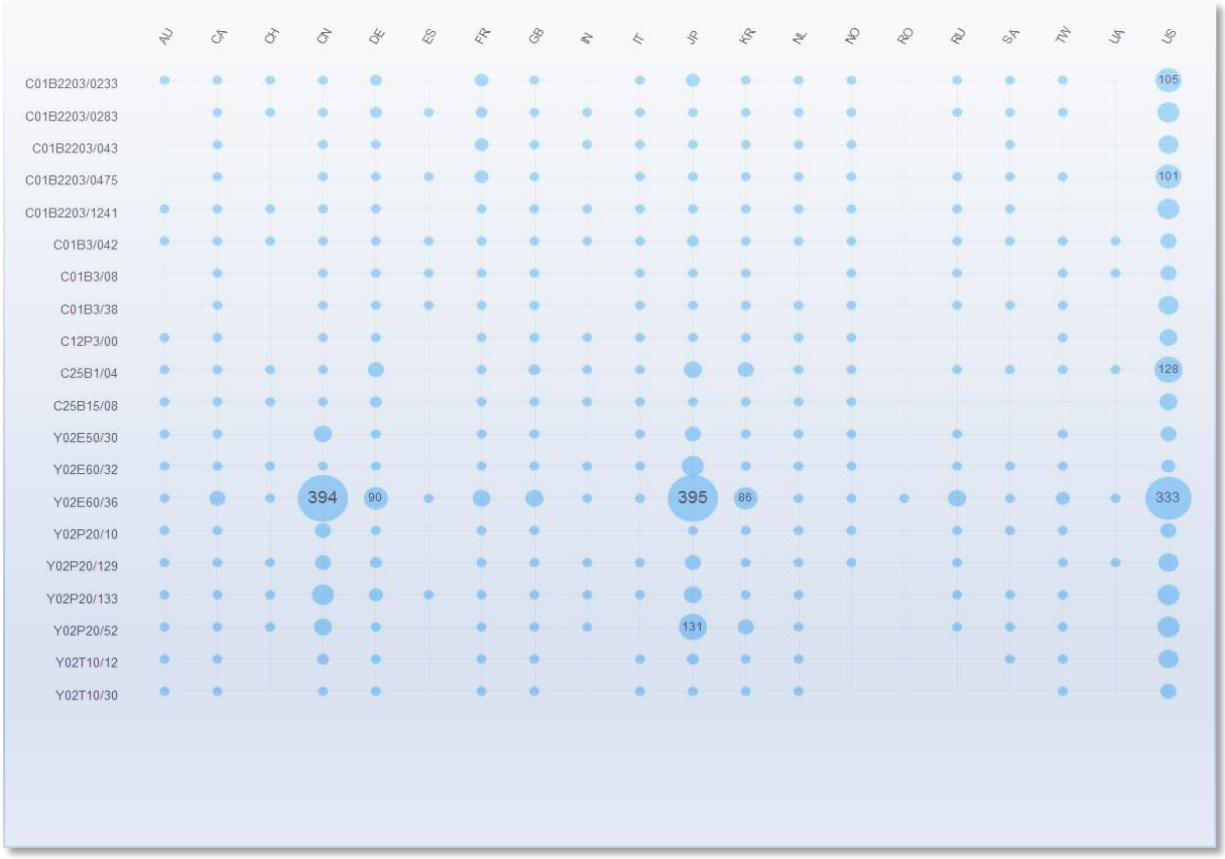


Figure 3.5: CPC codes versus country of inventor on patent publication

Tables 3.2 and 3.3 set forth the top 10 of respectively companies and academic institutions in the large data set. The large activity of China as shown in figure 3.4 is only reflected in the top 10 of academic institutions and only two Chinese companies are figuring in the top 10 of companies. It can thus be concluded that a significant portion of activity in patent filings with Chinese inventors is coming from academic institutions. Japan dominates the top 10 of companies and a bit surprising, the USA has only one company in the top 10. With Air Liquide there is also a representative from Europe in the top 10 of companies.

Table 3.2: top 10 of company patent publications

Company name	Number of patent publications
MITSUBISHI HEAVY IND LTD	92
TOSHIBA KK	80
TOKYO GAS CO LTD	54
DALIAN CHEMICAL PHYSICS INST	52
HONDA MOTOR CO LTD	49
AIR LIQUIDE	48
CHINA PETROCHEMICAL CORP	43
HITACHI LTD	43
TOYOTA MOTOR CO LTD	40
GEN ELECTRIC	39

Table 3.3: top 10 of academic institution patent publications

Name of Academic institutue	Number of patent publications
UNIV ZHEJIANG	62
UNIV TSINGHUA	57
KOREA ENERGY RESEARCH INST	44
UNIV SOUTHEAST	42
UNIV SOUTH CHINA TECH	40
HARBIN INST OF TECHNOLOGY	36
UNIV SHANGHAI	32
UNIV JIANGSU	32
UNIV FUDAN	30
UNIV EAST CHINA SCIENCE & TECH	30

4. Production of hydrogen from non-renewable sources

As set forth in section 2, a narrowed dataset of about 1350 patents was created within the large dataset used in the analysis in the preceding section 3 to examine the production of hydrogen from non-renewable resources in more detail.

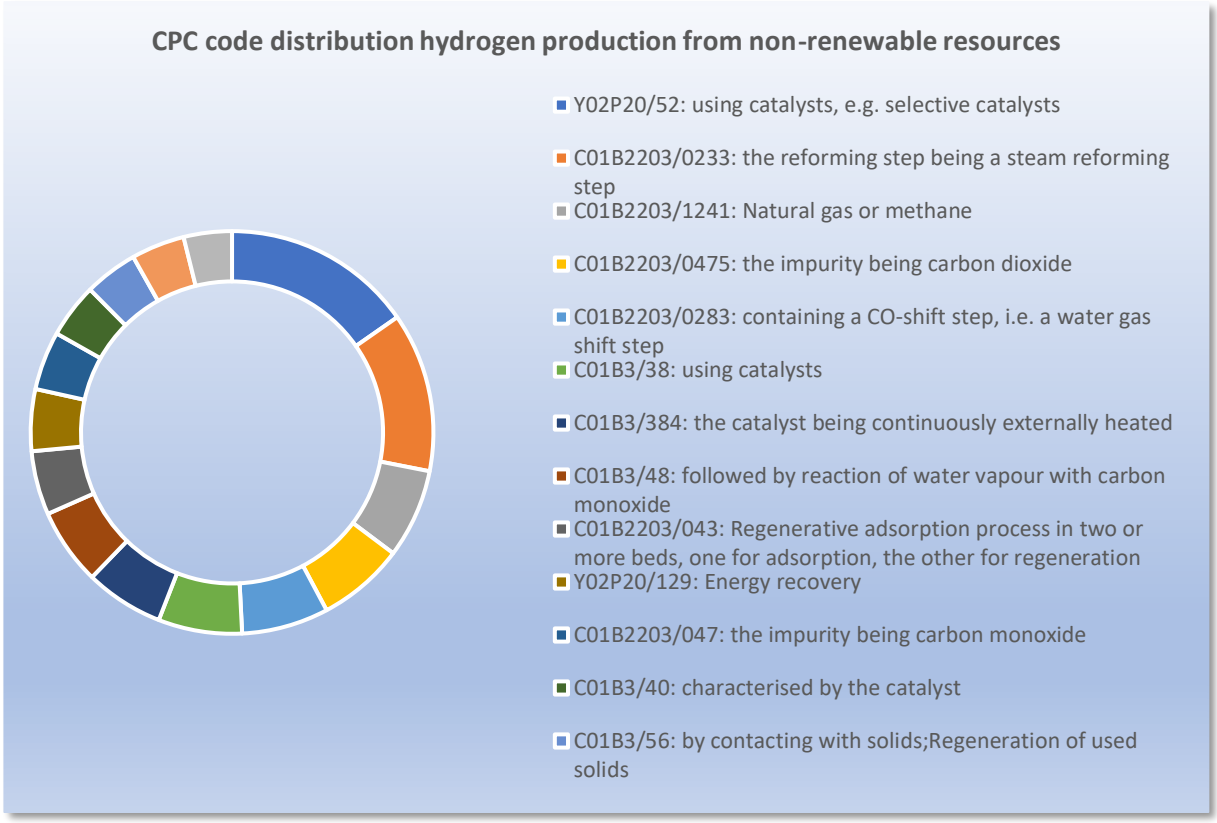


Figure 4.1 CPC classification code distribution for hydrogen production from non-renewable resources

Based on the CPC classification code distribution, a quick overview can be created on the main activities in the field of production of hydrogen from carbon containing resources. It can be seen that activity is going towards making the production less burdensome on the environment. Note in this respect the classes C01B203/0283, C01B2203/0475, C01B3/48 which are indicative of activity where carbon dioxide emissions are reduced.

Tables 3.1 and 3.2 set forth the top 10 of respectively companies and academic institutions with respect to production of hydrogen from non-renewable resources. The company top 5 is made out of Japanese companies and Air Liquide appears as European company in the top 10. Similar as for the overall dataset, the top 10 of academic institutions is largely Chinese.

Table 3.1: top 10 of company patent publications on production of hydrogen from non-renewable resources

Company name	Number of patent publications
MITSUBISHI HEAVY IND LTD	35
TOKYO GAS CO LTD	21
MITSUBISHI GAS CHEMICAL CO	20
OSAKA GAS CO LTD	18
TOSHIBA KK	17
AIR LIQUIDE	16
GUANGDONG HYDROGEN ENERGY SCIENCE AND TECHNOLOGY CO LTD	15
DALIAN CHEMICAL PHYSICS INST	14
CHINA PETROCHEMICAL CORP	13
ENGELHARD CORP	12

Table 3.2: top 10 of academic institution patent publications on production of hydrogen from non-renewable resources

Name of the institute	Number of patent publications
UNIV ZHEJIANG	15
UNIV CHENGDU TECHNOLOGY	12
UNIV SOUTH CHINA TECH	11
SNU R&DB FOUNDATION	11
UNIV SOUTHEAST	10
INST ENG THERMOPHYSICS CAS	10
KOREA ENERGY RESEARCH INST	10
UNIV WUHAN TECH	8
UNIV TSINGHUA	7
UNIV SUN YAT SEN	7

With the Patent Inspiration software a patent value analysis can be undertaken. With the patent value analysis, patents are scored based on the size of the patent family and the number of forward patent citations. A high score is obtained if the family is large and the number of forward citations is large. The size of the patent family can be taken as an indicator of the market significance of the patent. The number of forward citations is an indicator of the significance of the technology described. Using this analysis a set of patents was selected

for discussing the innovations in this area in more detail. The patents selected are set forth in table 3.3.

Table 3.3: selected patents based on patent value analysis relating to production of hydrogen from non-renewable resources.

Publication number	Publication date	Title	score	family size	number of citations
US2021189856A1	24 jun 2021	In-situ process to produce hydrogen from underground hydrocarbon reservoirs	56	19	0
US2010260657A1	14 okt 2010	Method and apparatus for hydrogen production and carbon dioxide recovery	57	6	22
US2010178219A1	15 jul 2010	Highly heat integrated reformer for hydrogen production	65	7	49
US2008267842A1	30 okt 2008	Process and apparatus for the production of useful products from carbonaceous feedstock	63	24	8
US2007011945A1	18 jan 2007	Systems and methods for producing synthesis gas	60	9	24
US2005207971A1	22 sep 2005	Low-temperature hydrogen production from oxygenated hydrocarbons	68	9	65
US2004172877A1	09 sep 2004	Compact steam reformer	60	8	31
US6059995A	09 mei 2000	Process and preparation of hydrogen-rich gas	60	7	44
US4091086A	23 mei 1978	Process for production of hydrogen	57	9	29
US4071330A	31 jan 1978	Steam reforming process and apparatus therefor	55	7	33

US 2021189856 is a patent of Proton Tech Inc., a US based company and relates to an underground hydrocarbon reservoir that is treated with heat to induce gasification, water-gas shift, and/or aquathermolysis reactions to generate gases including hydrogen. The hydrogen alone is produced to the surface by using hydrogen-only membranes in the production wells. The patent is still very young and thus has no forward citations. Nevertheless it has a high score due to the family size and is viewed important from a market perspective. Interesting to note is that the patent is from a US company which is not figuring in the top 10 of companies with the most patent publications in this field. It also illustrates the focus in this area of hydrogen production to reduce carbon dioxide emissions.

US2010260657 similarly is concerned with reducing carbon dioxide emissions and is from a Japanese company. The relatively large number of citations are indicative of the importance

of the technology disclosed in this patent which uses membranes to separate hydrogen from carbon dioxide.

US2010178219 has the second highest score and is related to a reactor for hydrogen production in distributed production facilities.

The patent with the highest score in the table (US2005207971) is also from a US applicant and relates to a method of producing hydrogen from oxygenated hydrocarbon reactants, such as methanol, glycerol, sugars or sugar alcohols. The method includes the steps of reacting water and a water-soluble oxygenated hydrocarbon in the presence of a metal-containing catalyst. The catalyst contains a metal selected from the group consisting of Group VIIIB transitional metals, alloys thereof, and mixtures thereof.

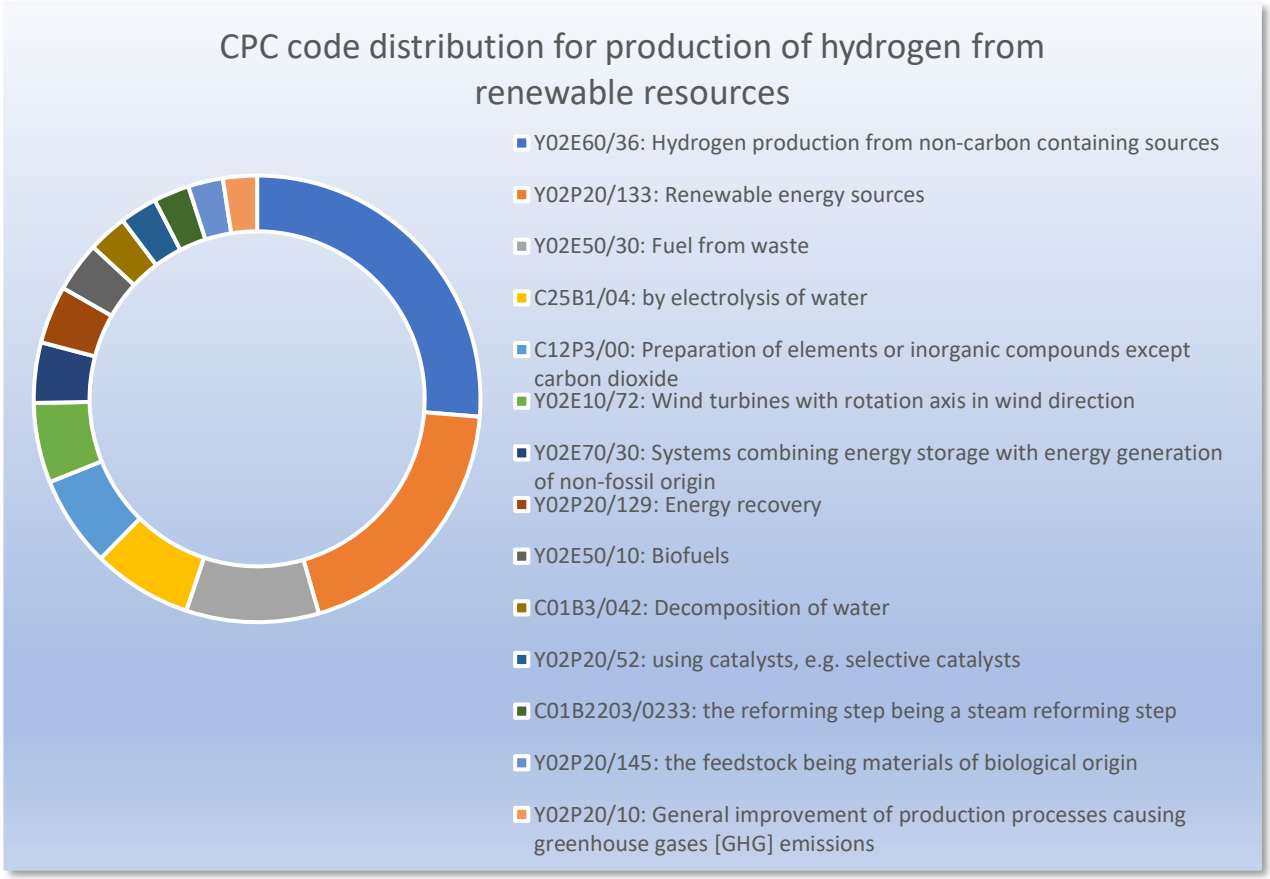
The last two patents in the table are from the end of the seventies and can be considered as early patents describing the technology of producing hydrogen through reforming. They are both cited relatively frequently and thus represent early patents that are technologically significant.

5. Production of hydrogen from renewable sources

The analysis of production of hydrogen from renewable sources was split over a dataset that was focussed on bio-based sources, renewable energy resources including sun and wind and a dataset targeting biological production of hydrogen through the use of micro-organisms.

5.1. Production of hydrogen using bio-based sources or renewable energy

Based on the CPC classification code distribution an overview was created on the main activities in the field of production of hydrogen from biobased sources and renewable energy production sources such as solar and wind. Figure 5.1.1 shows the CPC distribution



It can be seen that renewable energy sources (see Y02P20/133 and Y02E10/72) are the most explored activities in the field. Fuel from waste is an another important source. Biobased sources also are getting good attention in the research towards hydrogen production (classes Y02E50/10 and Y02P20/145). In common with the production of hydrogen based on non-renewable resources are catalyst research and steam reforming.

Tables 5.1.1 and 5.1.2 set forth the top 10 of respectively companies and academic institutions with respect to production of hydrogen from renewable resources.

Table 5.1.1 top 10 of company patent publications for production of hydrogen from renewable resources

Company name	Number of patent publications
DALIAN CHEMICAL PHYSICS INST	17
GUANGZHOU INST ENERGY CONV CAS	13
AGENCY INDUSTRIAL SCIENCE AND TECHNOLOGY	11
TOSHIBA KK	9
HONDA MOTOR CO LTD	8
SIEMENS AG	7
TOYOTA MOTOR CO LTD	7
GEN ELECTRIC	6
HITACHI LTD	6
NAT INST OF ADV IND & TECHNOL	6

Table 5.1.2: top 10 of academic institution patent publications for production of hydrogen from renewable resources

Name of academic institute	Number of patent publications
UNIV SOUTHEAST	15
UNIV ZHEJIANG	15
UNIV EAST CHINA SCIENCE & TECH	12
UNIV TSINGHUA	12
UNIV DALIAN TECH	9
UNIV HENAN AGRICULTURAL	9
UNIV JIANGSU	8
UNIV SHANGHAI JIAOTONG	7
UNIV XI AN JIAOTONG	7
HARBIN INST OF TECHNOLOGY	7

Comparing the top 10 list of companies in with the most patents in the field of hydrogen production from renewable resources with that of the top 10 of companies in the field of hydrogen production from non-renewable resources, it can be seen that the list differs significantly. The list for hydrogen production from renewable resources is headed by two Chinese companies followed by three Japanese companies. Also, numbers 2 and 3 on the list of hydrogen production from renewable resources did not occur in the list on hydrogen production from non-renewable resources. It can does be concluded that the research in the area of hydrogen from renewable resources is carried out by different players. Notwithstanding this, there are a number of players in common between the list but their ranking in the list is different.

In the top of academic institutes, we only find Chinese institutes. With the exception of 3 institutes, all institutes that are on the top 10 of hydrogen production from non-renewable resources are also found in the field of hydrogen production from renewable resources. Their rankings however differ. A comparison of their relevant rankings in the two lists may be indicative of their focus on the energy source in the production of hydrogen.

Using the patent value analysis a set of patents was selected for discussing the innovations in the field of production of hydrogen from renewable resources in more detail. The patents selected are set forth in table 5.1.3.

Table 5.1.3: selected patents based on patent value analysis in the field of production of hydrogen from renewable resources

Publication number	Publication date	Title	score	Family size	Number of citations
EP2983056A1	10 feb 2016	Solar photovoltaic power generation system provided with hydrogen production means	64	3	68
US2013289302A1	31 okt 2013	Methods and systems for generating polyols	62	24	4
US2011117006A1	19 mei 2011	Method and equipment for producing hydrogen from biomass	61	13	11
US2010003548A1	07 jan 2010	Recycling of waste material	63	20	9
US7352074B1	01 apr 2008	System for producing hydrogen making use of a stream of water	67	10	47
US2008006034A1	10 jan 2008	Method And System For The Recycling Of Municipal Solid Wastes, And Exploitation Of The Wasted Solid Recovery Fuel	73	23	28
US2007084502A1	19 apr 2007	Solar photovoltaic output for cloudy conditions with a solar tracking system	62	5	68
US6198037B1	06 mrt 2001	Solar battery module for optical electrolysis device and optical electrolysis device	62	10	36
US4011149A	08 mrt 1977	Photoelectrolysis of water by solar radiation	65	8	101

The technology of producing hydrogen from solar radiation goes back to at least the end of the seventies as shown by US 4011149, which is also the patent with the highest amount of citations. It shows the relevance of the technology disclosed in this patent to later developments. The patent relates to photoelectrolysis of water by solar radiation to produce hydrogen using semiconducting thin film electrodes.

The patent with the highest score is US 2008006034 relating to the use of waste as a source to produce hydrogen. The patent is from an Italian applicant and discusses a method and a system for the complete recycling of municipal solid wastes with minimal environmental impact and with the exploitation of the wasted solid recovery fuel for the production of electric energy and/or hydrogen. US 201003548 likewise uses waste to produce hydrogen in a gasification process.

US 2013289302 uses biomass as a source. The patent discloses methods for generating propylene glycol, ethylene glycol and other polyols, diols, ketones, aldehydes, carboxylic acids and alcohols from biomass using hydrogen produced from the biomass.

EP 2983056 is a patent from a Japanese applicant relating to the use of photovoltaic energy and efficiently converting this into hydrogen. US 2007084502 similarly is concerned with optimizing the conversion of photovoltaic energy into hydrogen.

Finally, US 6198037 concerns technology in which the electrolysis of an electrolyte is carried out by solar energy using a solar battery module in which multiple spherical solar battery elements are connected in series to generate the required electrolysis voltage.

5.2. Production of hydrogen using biological processes

An interesting method of producing hydrogen that is under development is the use of biological means such as micro-organisms, algae and fungi. As set forth in section 2, a dataset of about 350 patents related to this technology was created for further analysis. Using patent value analysis on this dataset the most interesting or relevant patents were selected and are set forth in table 5.2.1 below.

Table 5.2.1: selected patents based on patent value analysis relating to the use of biological energy sources

Publication number	Publication date	Title	score	family size	number of citatations
WO2015068054A1	14 mei 2015	Process for sequential bio-hydrogen production through integration of dark fermentation process with photo fermentation process	50	2	11
US2007042480A1	22 feb 2007	Process for producing hydrogen	67	9	24
US6942998B1	13 sep 2005	Process for generation of hydrogen gas from various feedstocks using thermophilic bacteria	64	7	27
US2005176131A1	11 aug 2005	Structured material for the production of hydrogen	53	2	35
US2005009159A1	13 jan 2005	Hydrogen production from organic wastes, manures and energy crops using a two-phase bioreactor system	50	1	41
US2004115782A1	17 jun 2004	Method and apparatus for hydrogen production from organic wastes and manure	53	1	59
US2004050778A1	18 mrt 2004	Method of producing hydrogen gas by using hydrogen bacteria	57	5	19
WO03067213A2	14 aug 2003	Modulation of sulfate permease for photosynthetic hydrogen production	52	6	9
US4480035A	30 okt 1984	Production of hydrogen	44	1	34
US4211621A	08 jul 1980	Method and apparatus for producing hydrogen using solar energy	52	7	11

US 2007042480 has the highest score and is from a Dutch applicant. The patent discloses a process that comprises the steps of introducing bio-oxidisable material into a reactor, which is provided with an anode and a cathode. The reactor contains anodophilic bacteria in an aqueous medium. Hydrogen is produced by applying a potential between the anode and

cathode and maintaining a pH of between 3 and 9. The hydrogen gas is collected at the cathode. The hydrogen production process can be intermittently switched to an electric power generation stage (biofuel cell) by adding oxygen to the cathode and separating the anode and cathode spaces by means of a cation exchange membrane.

US 2004115782 has the highest number of citations. This patent discloses a method for hydrogen production from biodegradable feedstocks. The feedstock is introduced into a first stage anaerobic bioreactor operating at thermophilic conditions to form a liquid effluent. The liquid effluent is then transferred through a plurality of hollow semipermeable fibers disposed in a second stage anaerobic bioreactor having a light transmitting wall. The hollow semipermeable fibers have an outer surface coated with a biofilm of photosynthetic bacteria. These photosynthetic bacteria generate hydrogen, using the nutrients in the hollow fibers and the incoming light.

The use of biological means goes back to the early eighties as illustrated by US 4480035 and US 4211621. The latter discloses a method in which an enzyme may be used to generate hydrogen in the claimed method. US 4480035 discloses a method in which hydrogen is produced from glucose with a hydrogen producing bacteria. Interestingly, the process also produces carbon dioxide which is separated from the hydrogen. The glucose may be obtained from a cellulosic biomass by enzymatic hydrolysis or otherwise. The process may be continuously run in a fermentation tank with the continuous feed of cellulosic biomass.

6. Photolytic water splitting to produce hydrogen

A further technology that is under development to produce hydrogen is that of photolytic splitting of water. Table 6.1 sets forth some of the interesting patents on this technology that were found with patent value analysis.

Table 6.1: selected patents using patent value analysis related to photolytic water splitting

Publication number	Publication date	Title	score	family size	number of citations
US2014342254A1	20 nov 2014	Photo-catalytic Systems for Production of Hydrogen	46	2	9
US2014301905A1	09 okt 2014	System for Harvesting Oriented Light - Water Splitting	39	4	1
US2012145532A1	14 jun 2012	Efficient hydrogen production by photocatalytic water splitting using surface plasmons in hybrid nanoparticles	56	2	34
US6063258A	16 mei 2000	Production of hydrogen from water using photocatalyst-electrolysis hybrid system	49	4	13
US4421617A	20 dec 1983	Photolytic production of hydrogen from water	61	15	9
US4382846A	10 mei 1983	Simultaneous production of hydrogen and oxygen from water	65	13	20
US4367131A	04 jan 1983	Photolytic production of hydrogen from water	62	16	10

Interestingly, the patents with the highest score date back to 1983 showing the technology has already a long history. US 4367131 and US 4421617 use a catalytic dispersion of fine metal particles to photodissociate water. US 4382846 discloses a method for the simultaneous production of hydrogen and oxygen from water by the visible light irradiation of a water solution containing photosensitizer, an electron relay and a suitable combination of redox catalysts. All three patents are from Engelhard Corporation, a US based company but the inventors were Swiss.

US2014342254 of Sunpower Technology LLC discloses a system for splitting water and producing hydrogen by using a photoactive material including photocatalytic capped colloidal nanocrystals (PCCN) and plasmonic nanoparticles. Through the photoactive material sunlight can split water into hydrogen and oxygen. US 2014301905 is also of Sunpower and uses a similar method employing polarized light.

US 2012145532 uses hybrid nanoparticles with metallic cores and semiconductor photocatalytic shells for photocatalytic water splitting. Efficient unassisted overall photocatalytic splitting of water is based on resonant absorption from surface plasmon in metal core/semiconductor shell hybrid nanoparticles, which can extend the absorption spectra further towards the visible-near infrared range, thus dramatically increasing the solar energy conversion efficiency.

Finally, US 6063258 discloses a hybrid method using photocatalysis and electrolysis. The method produces hydrogen gas from water by irradiating an aqueous solution containing ferric ions. The photocatalyst converts the ferric ions into ferrous ions that are then electrolyzed to yield a hydrogen gas.

7. Thermochemical water splitting to produce hydrogen

Hydrogen can also be produced by thermochemical water splitting. Also this method is being researched as a future method to produce hydrogen. Using patent value analysis on a dataset focussed on this technology relevant and representative patents describing the technology were selected. They are set forth in below table 7.1.

Table 7.1 selected patents on thermochemical water splitting

Publication number	Publication date	Title	score	family size	number of citations
US2012237440A1	20 sep 2012	METHOD FOR PRODUCING HYDROGEN BY MEANS OF THERMOCHEMICAL WATER-SPLITTING, AND DEVICE FOR PRODUCING HYDROGEN	50	4	4
US2012171080A1	05 jul 2012	SET-UP FOR PRODUCTION OF HYDROGEN GAS BY THERMO-CHEMICAL DECOMPOSITION OF WATER USING STEEL PLANT SLAG AND WASTE MATERIALS	56	12	1
US2011041740A1	24 feb 2011	RECUPERATIVE COMBUSTION SYSTEM	61	2	39
US2010136442A1	03 jun 2010	HYDROGEN PRODUCTION BY WATER DISSOCIATION IN THE PRESENCE OF SNO USING THE SNO2/SNO COUPLE IN A SERIES OF THERMOCHEMICAL REACTIONS	54	5	6
US2008256952A1	23 okt 2008	SOLAR POWER FOR THERMOCHEMICAL PRODUCTION OF HYDROGEN	53	2	21
GB2165532A	16 apr 1986	THERMOCHEMICAL HYDROGEN GENERATOR	60	5	22
US4391793A	05 jul 1983	PLANT FOR THERMOCHEMICAL WATER DISSOCIATION BY SOLAR ENERGY PLANT FOR THERMOCHEMICAL WATER DISSOCIATION BY SOLAR ENERGY PLANT FOR THERMOCHEMICAL WATER DISSOCIATION BY SOLAR ENERGY PLANT FOR THERMOCHEMICAL WATER DISSOCIATION BY SOLAR ENERGY	52	4	14
US3995012A	30 nov 1976	A METHOD OF PRODUCING HYDROGEN AND OXYGEN FROM WATER IN A THERMOCHEMICAL CYCLE	46	5	5
US3929980A	30 dec 1975	METHOD OF PRODUCING HYDROGEN	37	1	13

It is to be noted that the patents found have a relatively low score due to a low number of citations compared to patents found in previous sections. Also, the patent with the highest score and highest number of citations is relatively young, perhaps indicative that the more relevant developments have only recently taken off. That patent (US 2011041740) is on recuperating the heat of a combustion engine which is then used to thermochemically split water.

We have found some relevant patents on the technology dating back to the mid-seventies. In US 3929980, water is thermochemically decomposed to produce hydrogen by the following sequence of reactions. KNO_3 and I_2 are reacted to produce KI, NO and O_2. The NO and O_2 thus produced are reacted with water to form HNO_3. A hydrogen-containing iodide - NH_4I or HI - is formed from the HNO_3, and this iodide is thermally decomposed to produce hydrogen. All products of the reactions are recycled except hydrogen and oxygen.

US 3995012 is a patent from the nuclear research institute in Juelich, Germany. The patent relates to a method of producing hydrogen and oxygen by splitting water in a thermochemical cycle, according to which in a first method stage a gas mixture of from 1 to 50 parts by volume of steam and 2 parts by volume of sulfur dioxide is reacted at a temperature within the temperature range of from 200 ºC to 400 ºC with an oxide of one of the metals manganese, iron, cobalt, nickel, zinc or cadmium for forming a metal sulfate and for freeing hydrogen gas.

GB 2165532 of General Electric Company discloses a thermochemical hydrogen generator based on a metallic hydride and an ionic hydride.

US 2008256952 discloses the use of solar power to thermochemically split water. Solar energy is also used in US 2012237440 to thermochemically split water.

Finally, US 2012171080 relates to the production of hydrogen by decomposing water using steel plant slag and waste material. The system uses a graphite crucible containing molten slag and a reaction hood disposed over the crucible. Water is sprayed on the molten slag in the crucible. Hydrogen is produced by the thermal splitting of water and the so generated hydrogen is collected in a steel tube that then transfers the hydrogen to into a condenser tank.