JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

Artificial photosynthesis and current status of its application in generating fuels: A patent analytical study

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Abstract:

Scientists around the world are working towards the goal of developing technologies to make use of energy from the sun to produce fuels for transport, industry and electricity generation. Fuels produced using solar energy and carbon dioxide from the environment would transform our energy options in the future by providing an alternative to fossil fuels.

This report analyses the artificial photosynthesis technology for producing fuels through the lens of intellectual property. It uses the scale and intensity of patent activity to provide an overview of innovation in this technology.

This study identified 53 innovations related to artificial photosynthesis. These results were categorized into four broad technology sub classes according to the type of system or area for fuel production and then analyzed to give a picture of the landscape in this area of research.

The applicants that made major contributions to this field have origins from the United States of America, Korea and Japan, whereas Israel, Spain, Russia has had nominal patent involvement in the contribution

to this field of study. Study on analysis of patent commercialization reveals that very few patents are exploited commercially.

Keywords: Artificial photosynthesis, renewable energy sources, Patents, sustainable energy

Declarations/ Conflict of Interest: There is no conflict of interest

Funding: 'Not applicable'

Introduction

Artificial photosynthesis is a term which describes the processes that, like natural photosynthesis, harvest sunlight and use this energy to chemically convert water and carbon dioxide into fuels [1]. The journey began in the 19th century with the discovery of the 'photovoltaic effect', whereby an electric current is produced in a material when exposed to light.

Scientists around the world are working towards the goal of developing technologies to exploit energy from the sun to produce fuels for transport, industry and electricity generation. Fuels produced using solar energy would transform our energy options in the future by providing an alternative to fossil fuels [2].

The purpose of this report is to explore the patent landscape of artificial photosynthesis technologies, specifically in the areas of solar energy harvesting and carbon dioxide reduction for the production of fuels.

The main focus of this report will be to investigate global patent trends within these technologies and more specifically to identify who is filing patent applications and where.

Another aim of this report is to see if the use of sunlight and atmospheric carbon dioxide for production of fuels as an emerging technology to solve the challenges of meeting the growing demand of fuel supply.

Patents can be used as indicators of research output. A patent is a right that is granted for any device, substance, method or process that is new, inventive, and useful Patent rights are legally enforceable and give the owner exclusive rights to commercially exploit the invention for a limited period of time.

It is a requirement of patent law that patent documents are published and that they fully disclose inventions. As a result of the disclosure requirement, patent literature reflects developments in science and technology. Patent documents include other useful information, such as international patent classifications and information about inventors and applicants.

Through the extraction and analysis of data associated with patent documents, it is possible to measure aspects of inventive activity such as scope, intensity, collaboration and impact. These metrics can be

developed across technology sectors and by various units of measurement, such as individuals (inventors), institutions (applicants), regions and countries. The above groups were manually classified sorted and provide more useful analysis than the IPC. The IPC was not suitable for our analysis, as the artificial photosynthesis technology is interdisciplinary.

Methodology

A patent landscape report is a comprehensive analysis based on patent documents in a specific technology area, covering global patenting activity or patenting in a certain geographical area. The first step in preparing such a landscape report is to understand the main objectives and the technology scope. The main objectives usually lead to a series of more specific questions to be addressed. The technology area is usually broken down into sub-areas representing various technical aspects. Next a state -of-the -art patent search is performed to collect relevant patent information. The patent search results are then analyzed to provide answers to those questions regarding the main objectives.

Search strategy and data formatting

We searched the Thomson Innovation database for patents relating to artificial photosynthesis for the period from 2002-2019. Following query was fired to obtain the data.

Search Query

1. CTB=(ARTIFICIAL PHOTOSYNTHESIS) OR CTB=(MIMICKING PLANTS FOR FUELS) AND CTB=(NANOMATERIALS);

2. CTB=(ARTIFICIAL ADJ PHOTOSYNTHESIS) OR CTB=(converting ADJ solar ADJ energy ADJ in ADJ to ADJ fuels) AND CTB=(SUNLIGHT);

3. CTB=(REDUCE ADJ CARBONDIOXIDE) AND CTB=(SUNLIGHT) AND CTB=(FUELS)

All the patent data was sorted according to relevance of topic and compacted into simple patent families [3]. A separate Excel sheet was prepared that includes all relevant simple patent families. Each simple family was identified and represented by the publication number of a single published family member,preferably the earliest published PCT publication number [4], if available. If the family has no PCT family member, the family member published in English was selected.

The patent data included the following bibliographic information for each family. Title

- Abstract
- Claims
- Applicant/assignee name(s)
- Inventor name(s)

- Priority information
- Earliest priority date (or application date in case no priority is claimed) , i.e. the date of first filing in the family
- Priority country of earliest priority
- Publication numbers of all members of the simple family
- IPC symbols
- Number of forward citations
- No. of backward citations
- Status of patent (Dead/alive)

The search results were categorized into the following groups

1. Artificial photosynthesis modules: patent families including systems which are used to convert water and carbon dioxide in to different types of fuels.

2. Photocatalysts: patent families including photocatalyst which are used to produce fuels using sunlight.

3. Photo-electrochemistry: patent families including electrochemical generation of fuels from water and carbon dioxide using sunlight.

4. Nanomaterials: patent families including nano-sized metal or metalloid particles used for generation of fuels from water, carbon dioxide or sunlight

The above groups were manually classified sorted and provide more useful analysis than the IPC. The IPC was not suitable for our analysis, as the field of artificial photosynthesis is more interdisciplinary.

Publication trend

Figure 1: Year wise Publication Trend of patents in the Artificial Photosynthesis technology

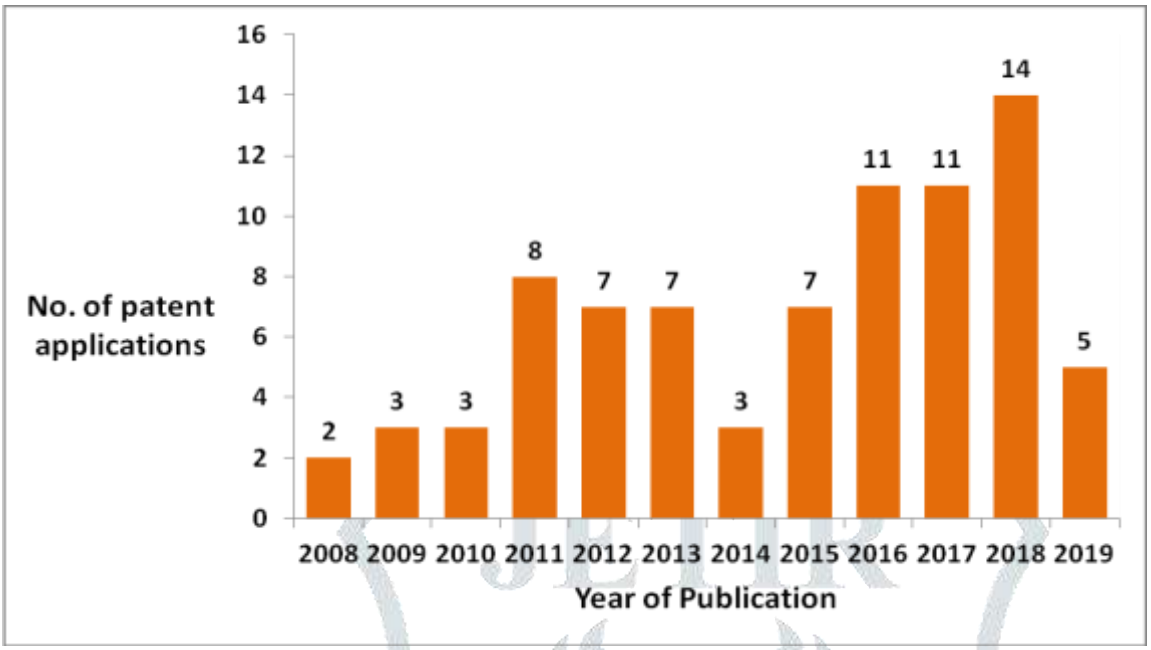


Figure 1 demonstrates the artificial photosynthesis patent applications over the period 2008-2019.

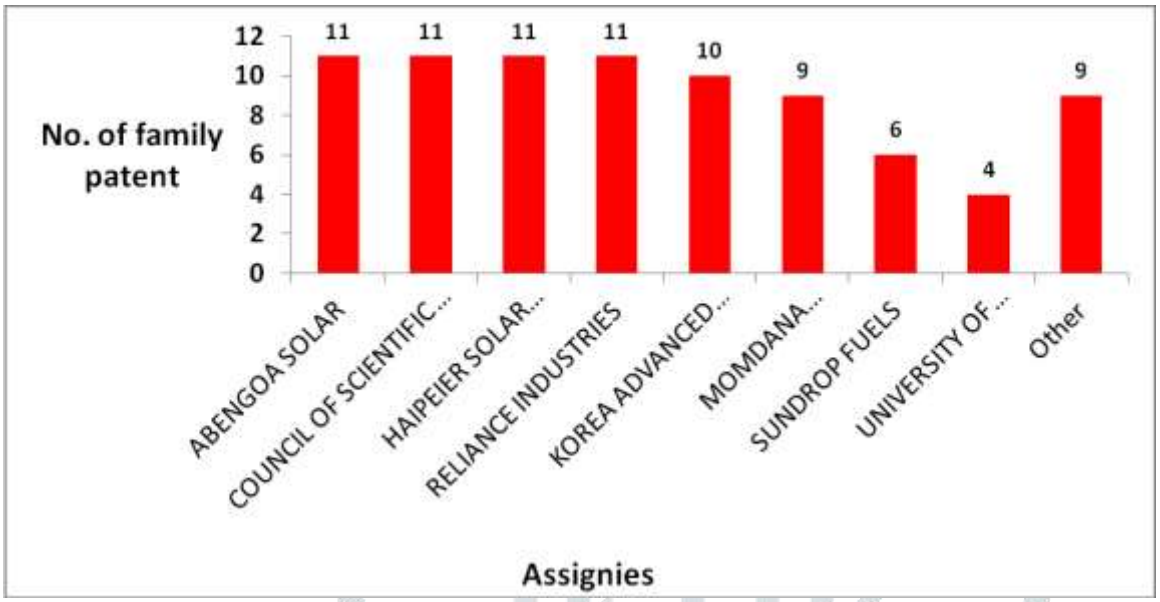
There has been steady work around this area throughout the last few decades but the real flow in the activity around this technology has happened in the year 2011-2018.

The total number of patent family applications per year in the field of agricultural nanomaterials has steadily increased from two patent applications in 2008 to 14 patent applications in 2018. In the year 2014 saw fewer publication of artificial photosynthesis patent applications, however from the 2015 onwards again growth in publication of patent applications was seen. The highest patent applications were published in 2018. The growing demand for fuel as well the global emphasis on reducing emissions and recycling of gaseous pollutant to save environment may have contributed to this more recent growth in patent filings.

Top assignees

From the 53 patent families related to artificial photosynthesis, 14 distinct applicants were identified. Figure 2 shows the top ranked applicants in this area. ABENGOA SOLAR, HAIPEIER SOLAR ENERGY HYPERSOLAR SAEED MUBIAN and COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH in collaboration with RELIANCE INDUSTRIES are the most active applicants, each with 11 patent family members.

Figure 2: Top Assignee



ABENGOA SOLAR is a subsidiary of Abengoa headquartered in Spain, is a multinational chemical company whose portfolio includes the development of photovoltaics, concentratedphotovoltaics, or concentrated solar thermal technologies. ABENGOA SOLAR has patent families in the area of Photo-electrochemistry, and the most recent patent family has a priority date in 2008. In particular, WO2009095509 relates to liquid Low concentration solar plant and method for maximizing the electricity production of the photovoltaic modules thereof. This patent family has 11 applications.

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH and RELIANCE INDUSTRIES are India based Government Research organization and an Indian private sector enterprise respectively. RELIANCE INDUSTRIES is involved in power generation, infrastructure, construction and defense. They have eleven patent family in the area of photo-electrochemistry and have priority date in 2011 with PCT publication WO2013046228 related to process for generation of hydrogen and syngas. KOREA ADVANCED INSTITUTE OF SCIENCE & TECHNOLOGY is a Korean Institute, has ten patent family members in the area of photocatalyst related to production of formic acid.

MONTANA STATE UNIVERSITY is a US based research Institute, has nine patent family members relating to Composite Nanomaterial for photocatalytic hydrogen production particularly PCT publication WO2013046228 relates to reaction for fixation of anthropogenic CO2 into calcium carbonate using carbonic anhydrase (CA) as a biocatalyst.CA is being employed to accelerate the rate of hydration of CO2 to form carbonate ions and proton. SUNDROP FUELS is US based bio-based fuel and chemical company, with headquarters in Longmont, Colorado has six patent family members with priority in 2010. More particularly PCT publication number WO2010036662 related to the products from a solar

assisted reverse-water-gas-shift reaction (RWGS) are used to create a liquid hydrocarbon fuel. A synthesis reactor uses any unconsumed hydrogen molecules and the resultant stabilized carbon monoxide molecules from the RWGS reaction in the hydrocarbon fuel synthesis process to create a liquid hydrocarbon fuel.

UNIVERSITY OF COLORADO again a public research university located in Boulder, Colorado, United States has four patent family members with priority in 2013.

Other major applicants are HIROYUKI KOBAYASHI, UCHICAGO ARGONNE, ZHEJIANG GONGSHANG UNIVERSITY, ZHEJIANG GONGSHANG UNIVERSITY, GOVERNING COUNCIL OF THE UNIVERSITY OF TORONTO collectively have nine patent family members.

Top filling country

Although ABENGOA SOLAR (Spain), and COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH in collaboration with RELIANCE INDUSTRIES (India) are the applicants with the largest number of patent family members, the United States is the country with the most applications. Figure 3 demonstrates top filling applicant origin. The top three countries hold almost 50 per cent of the total patent families.

The United States is a highest patent filling country in the field of artificial photosynthesis. Korea is the second largest filling country. Japan China, ranked third overall.

Figure 3: Top filling countries in the Artificial Photosynthesis technology

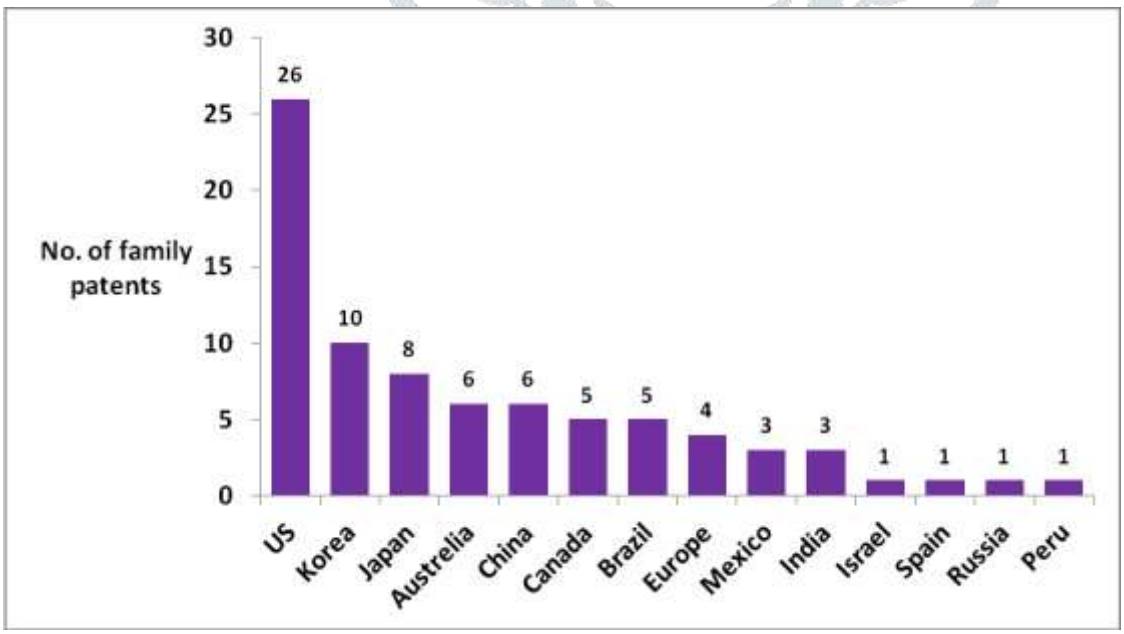
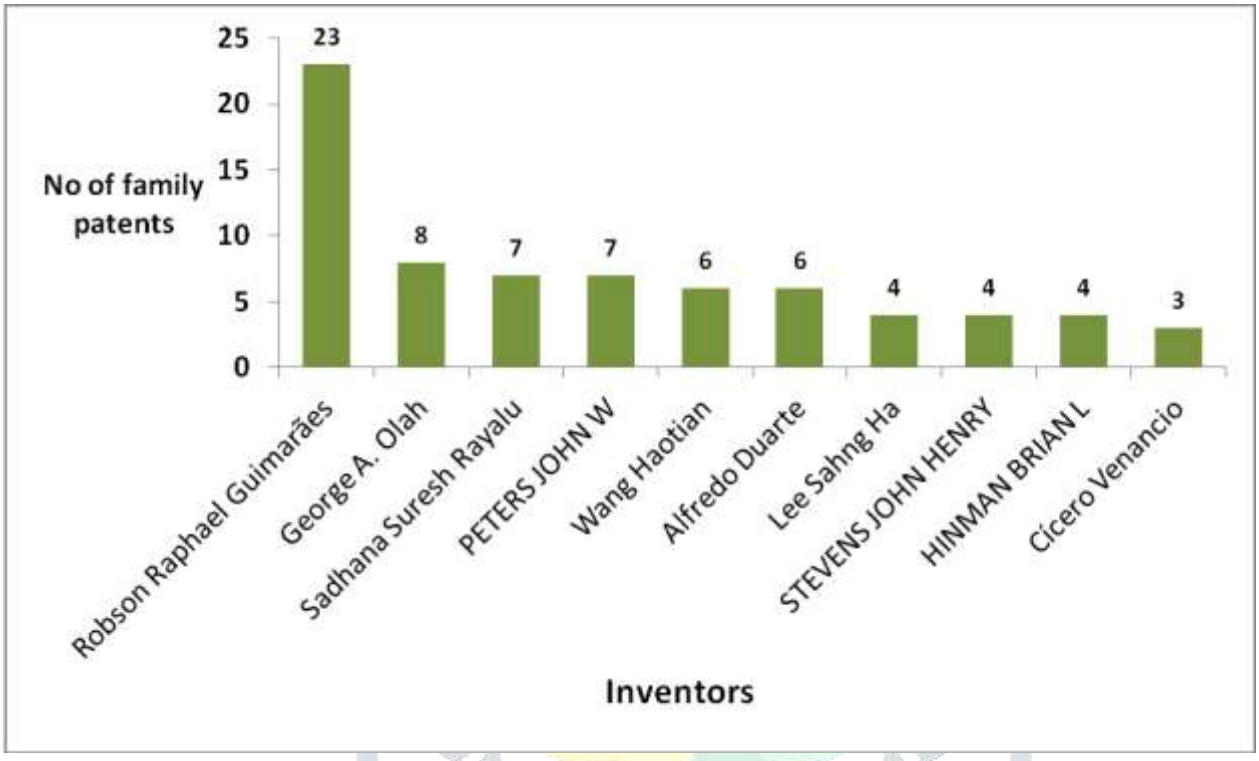


Figure 3 also shows that the remainder of the world are not patenting in large numbers in the area of artificial photosynthesis. Israel, Spain, Russia and Peru contribute list patents in the field of artificial photosynthesis.

Top inventors

An analysis of the inventors of the 53 patent family members identified about twelve productive Inventors with at least three patent family members.

Figure 4: Top inventors in the Artificial Photosynthesis technology

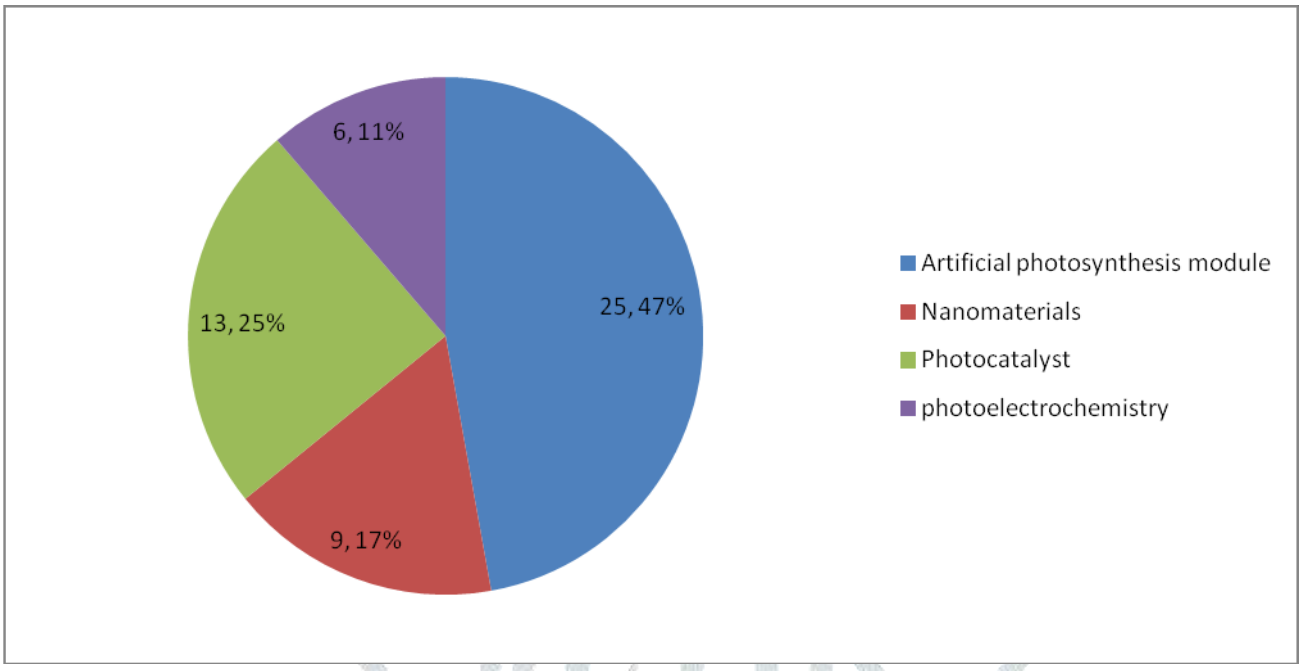


ROBSON RAPHAEL GUIMARÃES was the leading inventor with 23 family patents filed across various countries. GEORGE A. OLAH was the second leading inventor, involved in eight family patents. SADHANA SURESH RAYALU and PETERS JOHN W were the third leading inventors, involved in seven patent inventions. Inventors WANG HAOTIAN, ALFREDO DUARTE were the next leading inventors with each of them having six patent family members. Lee Sahng Ha, STEVENS JOHN HENRY and HINMAN BRIAN L involved in four patent family members each and CÍCERO VENANCIO having three patent family members.

Technology sub-area analysis

The technology artificial photosynthesis was divided further in four sub-groups as shown in Figure 5. Each patent family was assigned a technology sub-area based on the type of fuel produced and the type of technology by reviewing the abstract and description associated with each of the patent families.

Figure 5: Share of various sub-areas in the artificial photosynthesis technology



An in-depth analysis of various areas related to artificial photosynthesis revealed that the "Artificial photosynthesis module" is the predominant area in artificial photosynthesis. The "Artificial photosynthesis module" accounts for 47% (or 25 patent family members) out of 53 patent family. The inventions classified in this category relates generally to modules for reduction of atmospheric carbon dioxide and water into fuel specifically, to carbonaceous fuel by utilizing sunlight.

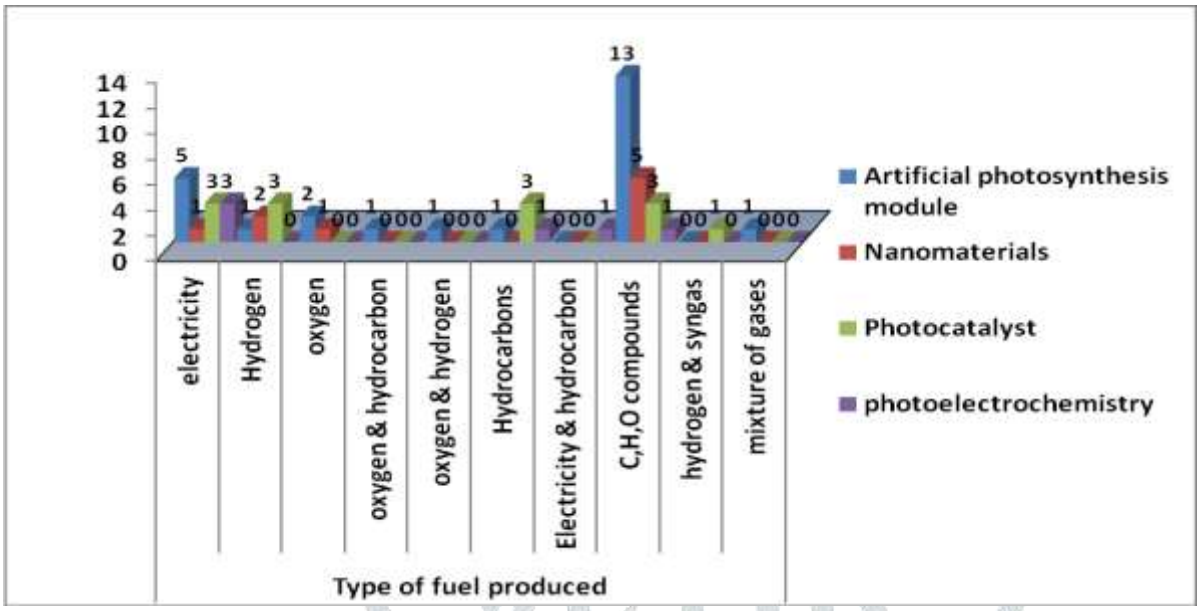
The second most important technology is that of "Photocatalyst", which is disclosed in

13 patent families (accounting for 25% of the total 53 patent family members). All these patent family employed metal, metalloid and non-metals as catalyst for capturing the sunlight i.e. conversion of sunlight in to different types of fuels. Yet another 9 patent family disclose "nanomaterials" particularly Metal nanoparticles including bismuth, nickel cobalt serves as a charge carrier which enhances the photoefficiency of the solar cells. Semiconductor Nanomaterial including silicon nanowires, Titanium oxide, shere shaped carbon-nitride nanoparticles again acts as efficient catalyst for reduction of carbondioxide. Graphenenanomaterials have major contribution in the field of catalyst of solar energy conversion.

The "photo-electrochemistry" is another area which disclosed in six patent family members (11% of 53 patent family members); which relates to the photo-electrochemical conversion of solar energy into fuel energy with high efficiency by using CO_2 and water as starting materials.

Analysis based on type of fuel produced

Figure 6: Type of fuel produced in various sub-areas of the artificial photosynthesis technology



The obtained 53 patent family member were further sub-grouped on the basis of the type of Fuel produced by each of technology sub-area. Among 53 patents family carbon- hydrogen-oxygen compounds dominated the entire portfolio. As indicated on the graph,

13 out of 53 patent family members refer to the carbon-hydrogen-oxygen compounds under artificial photosynthesis module sub-area. It includes the alcoholic compounds such as methanol, ethanol which are used as additive for fuel or directly as fuel.

Other types of fuels including electricity, hydrogen, oxygen, hydrocarbons, mixture of gases are spread across all four technology subarea. There are 12 patents family which refer to the production of electricity collectively belongs to all four technology subarea. Remarkably, PCT publication WO2009095509 has total twelve family members, the invention related to low concentration solar plant and method for maximizing the electricity production of the photovoltaic modules. Hydrogen is the third leading fuel contributing six patent families. PCT publication WO2007086918 has nine family members across the world generally related to reaction of an electron donor with a composite material for photocatalytic hydrogen production by utilizing 1) a polymer gel;

2) a photocatalyst; and 3) a protein based H_2 catalyst. Hydrogen is one the major fuel product produced during photoelectrochemical decomposition of water.

Syngas and mixture of gas has less contribution to the technology, however these products are utilized for the production of hydrocarbons and alcoholic compounds [5].

Legal status of patents and technology commercialization analysis

Status of patent application is a proxy for assessment of commercialization of technology. Figure 7 indicates the legal status of the patents irrespective of countries they are filed. Out of 53 patent families across the world 39 patent families are in force. There are 14 patent families which are lapsed due to fees related issues or not being commercialized.

Figure 8 shows patent applications in major countries which are in force or dead at the date of conducting that patent search. By analyzing the numbers of patents still in force in these countries, it is possible to get a picture where the applicants consider the biggest markets for the inventions.

Figure 7: Legal status

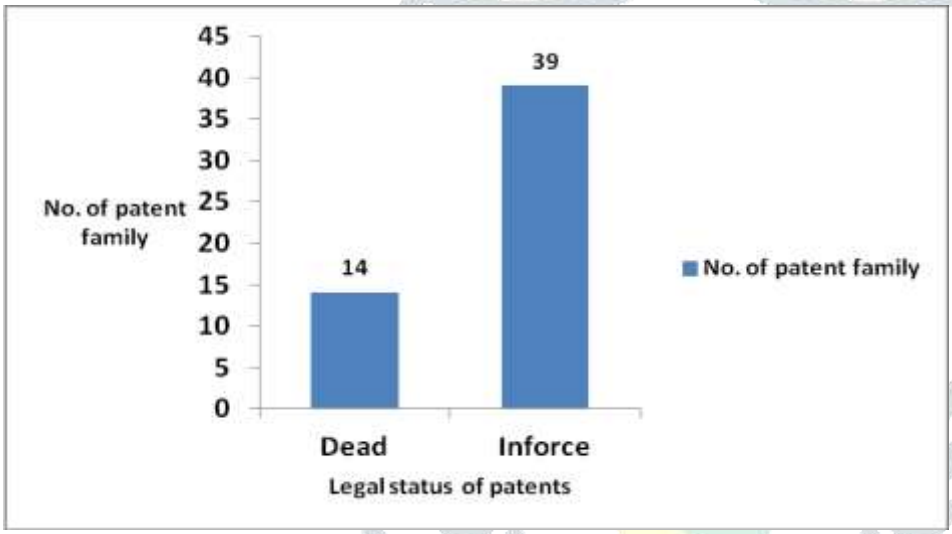


Figure 8: In Force and Lapsed patent applications since 2002

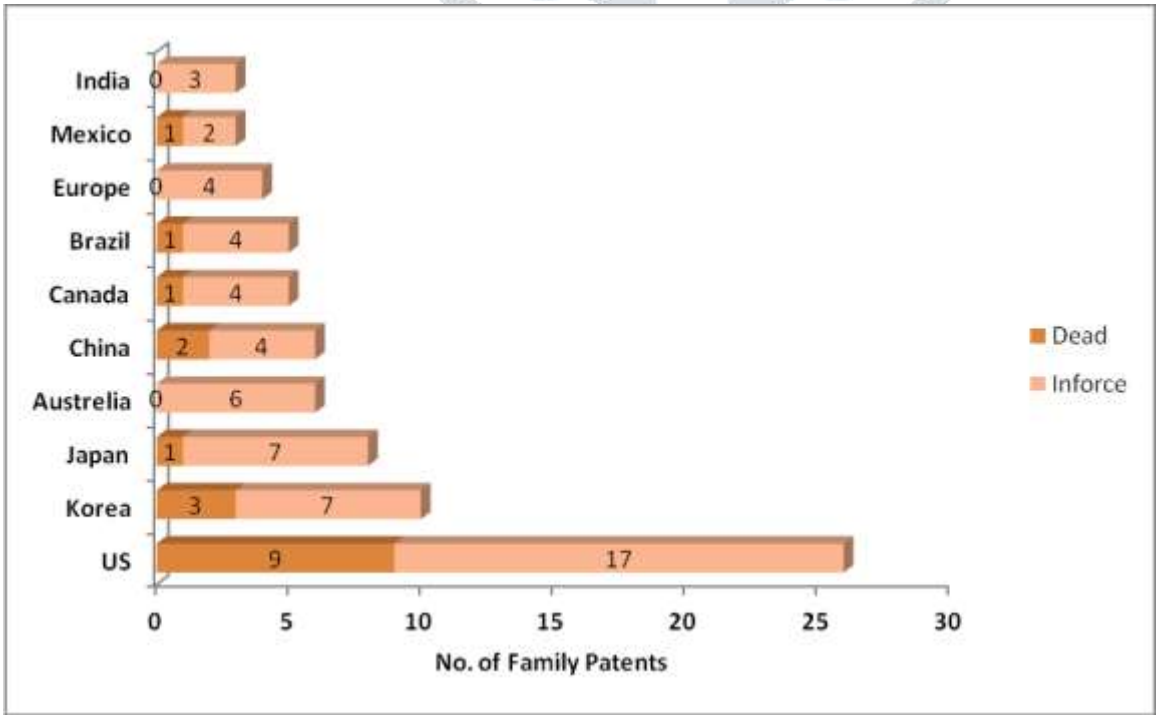


Figure 8 indicates that applicants are primarily protecting their inventions in the United States, Australia and Korea. Overall almost all major filing countries have kept their patents in force. As artificial Photosynthesis is an immerging technology therefore, it is challenging to move laboratory prototype systems to commercial technologies. However, if this new route of producing fuels is achieved on a large scale, it would transform our sustainable energy options by providing alternatives to oil, gas and coal as sources of fuel for transport, industry and electricity generation [6].

Scientists and engineers are working together on significant scientific and technological challenges to successfully scale up laboratory prototypes to a commercial scale [7]. PCT application number PCT/US2006/013742 having priority from US is a single patent family which is commercialized till date. It has nine patent family members across the world. The patent is related to the reduction process for converting CO_2 into methanol with the help of Nobel Laureate George A Olah (Inventor) [8]. The company CRI (Carbon Recycling International) George Olah Plant is located at Iceland. It has capacity of producing 5 million Liters of Methanol per year in the year 2015-2016. The recycling capacity of the plant is 5.5 thousand Cubic Meters of carbon dioxide per year. However, it took around 10 years to commercialize the technology [2006-2015(calculated from filling date)]. Further analysis revealed that there is no licensee for this technology [9].

Korea is second major filling country. The Korean Centre for Artificial Photosynthesis (KCAP) was launched at Sogang University in 2009, Funded by the National Research Foundation of Korea, it is working on materials development for photo-electrocatalysis and the development of systems for artificial photosynthesis, thus have both basic research and technical development with the goal of commercial exploitation[10]

There are programs dedicated to artificial photosynthesis research and innovation in the United States, the Netherlands and South Korea, as well as renewable energy research centers in China and Japan.

Recently, the US Department of Energy (DOE) set up three Energy Innovation Hubs, including a solar research facility. In July 2010, the DOE awarded $122 million dollars over five years to researchers at California Institute of Technology in partnership with the DOE's Lawrence Berkeley National Laboratory for the formation of the Joint Center for Artificial Photosynthesis (JCAP). The preliminary objective of JCAP is to rapidly move artificial photosynthetic research out of the laboratory setting for commercial exploitation

[11].

There is also evidence of some industries like RELIANCE INDUSTRY, SUNDROP FUELS investing in artificial photosynthesis fuels research and innovation [12,13].

Major limitations on the practical application and commercial use of approaches to artificial Photosynthesis technology

1. Scalability of the invention is major obstacle to successful implementation of technology on commercial scale specifically with regard to photoelectrochemistry (electrolysers).

2. The area required for "light harvesting" is second major challenge.

3. On a larger scale, difficulties to store, distribute, and use hydrogen.

4. Higher cost of development and design of architectures which can be used for scaling- up from the small scale to large scale [14]

Conclusion

This report uses the scale and intensity of patent activity related to synthesis of fuel from sunlight and carbon dioxide using artificial photosynthesis technologies to provide an overview of innovation in the area. The report analysis on 53 patent families related to artificial photosynthesis, is concluded as below

1. Patent activity in the field has increased since the year 2011. A noticeable increase in patent families in the technology sub area of Artificial photosynthesis module and Photocatalyst has largely contributed to this.

2. Almost half of the patent families were in the category of Artificial photosynthesis module primarily on production carbon hydrogen and oxygen type of compounds.

3. In the area of Photocatalyst, the major technology focus was in improving production of hydrogen, hydrocarbon and carbon hydrogen and oxygen type of fuels with 13 patent families.

4. By identifying the origin of the applicants of patent families, the jurisdictions providing the majority of contributions to the field of study were determined. The majority of contributions arise from the United States of America, Korea, Japan and Australia. However, only one patent family originates from Israel, Spain, Russia and Peru.

5. This report identified few collaboration in the patent area includes collaboration between COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH and RELIANCE INDUSTRIES. The major patent filling assignees such as HAIPEIER SOLAR ENERGY HYPERSOLARSAEED MUBIAN UNIVERSITY OF CALIFORNIA and KOREA ADVANCED INSTITUTE OF SCIENCE & TECHNOLOGY found to exhibit a collaboration using the methods of this study.

6. The major markets are the United States of America and Korea, these countries had the highest proportion of patents still in force.

7. Carbon-Hydrogen_Oxygen containing fuel contributes more to the technology followed by electricity and hydrogen. However, very few patents were commercialized at industry level.

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