CONVERSION OF BIOMASS TO HYDROGEN USING PYROLYSIS

A DISSERTATION
Submitted in partial fulfilment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(With Specialization in Computer Aided Process Plant Design)

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CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented in this dissertation entitled "**CONVERSION OF BIOMASS TO HYDROGEN BY PYROLYSIS**", in partial fulfillment of the requirement for the award of the degree of **Master of Technology** in **Chemical Engineering** with specialization in "**COMPUTER AIDED PROCESS PLANT DESIGN**", submitted in the **Department of Chemical Engineering** of **Indian Institute of Technology Roorkee**, Roorkee is an authentic record of my own work carried out during the period from June 2005 to June 2006 at Indian Institute of Petroleum, Dehradun, under supervision of Dr.H.B.Goyal, Scientist 'F', Dehradun, Dr.V.K.Agrawal, Associate Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee.

The matter embodied in this dissertation work has not been submitted for the award of any other degree.

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CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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Abstract

Energy demand and consumption has increased tremendously with the increase in the population and industrialization. Even the developed countries are unable to cope up with the energy demands. Most of the energy required comes from fossil fuels. There are two major problems that every country is facing today. Firstly these fossil fuels are at the verge of getting extinct. It is expected that these may deplete by the year 2030. Another problem related to the environment. Production of energy from the fossil fuels leads to environmental pollution. Global warming, green house effect, depletion of ozone etc. are some of the problems that every nation is facing. Emissions from the combustion of fuels are the nuisance creating substances.

There is need of some alternate fuel which will not only be a good substitute for the fossil fuels but also be environment friendly. Lot of renewable fuels is considered for this like wind, water, sunlight etc. usage of these alternatives is costly affair for the common man. So the fuel or the energy should be from a cheap source. The best suitable found was the biomass. It is cheap and also easily available. Biomass has been used from ancient times. But the process of obtaining energy is not efficient and also harmful to the environment. Biomass if converted to a better fuel using processes like pyrolysis or gasification can be a good substitute to the fossil fuels.

Hydrogen could be a fuel for the future as it has high calorific value and is the cleanest fuel. The conventional methods of preparation of hydrogen are very costly. Converting biomass into hydrogen could help in the reduction of prices of the hydrogen to be used as fuel. Processes like pyrolysis and gasification are the important routes for this. These are all high temperature reactions whereby require a suitable reactor and other equipments. In this report a mechanical design of a reactor and furnace parts are reported which is essential for the production of hydrogen from biomass at high temperatures. Suitable insulation kinetics is also covered to get the best of heat exchange and transfer. This design will help in increasing the quality and the quantity of the products.

The report also covers the preparation of the catalysts to be used in the process. This also provides the schematic description of the bench scale unit and also covers the pretreatment and pre-analysis of biomass.

This report is made keeping in mind to obtain a appropriate reactor system which will help to give high yields and thereby reduce the overall cost of the hydrogen.

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CHAPTER 1

INTRODUCTION

1.0 INTRODUCTION

The importance of "energy issues' has been recognized worldwide, especially after the first and second oil shocks in the 1970s. Then, considerable efforts to diversify energy resources such as coal, natural gas and nuclear power as well as to promote energy saving measures were taken in developed countries. However, more than ever, global warming caused by greenhouse gases has been newly recognized worldwide around the turn of the new century. Due to remarkable population growth and improvement in living standards in developing countries, energy demands are expected to increase rapidly in the near future. This will lead to serious environmental disruption. We have to do our best to enable sustainable development of human civilization without the violation of global environment. We must all consider this critical issue for the betterment of the future.

Energy mainly depends upon the fossil fuels like crude oil, natural gas & coal. Now, the present scenario of continuous hike in the price of crude oil (73$per barrel) signifies the growing extinction of oil reserves. The details regarding the geographical distribution of crude oil and natural gas reserves across the globe are listed in table 1. [46] Another growing menace to the society is environmental pollution. All fuels are getting checked for least emission of gases causing global warming, as per pollution regulation norms. Though the present energy demands are getting met with the existing fossil fuels, alternate fuels are in the major hunt since 1970 for their effective and efficient utilization leading to an economical and eco-friendly world. Hydrogen is under active research for the same owing to its high calorific value, easy availability & suitable physical and chemical properties.

Hydrogen is not a primary fuel; it is already being produced from fossil fuel sources such as natural gas, naphtha and coal. Hydrogen is potent to be a clean alternative to the fossil fuels currently used in the transportation sector. This is more pronounced with the hydrogen produced from renewable resources, primarily sunlight, wind and biomass.

Analyses have been conducted to assess the economic feasibility of producing hydrogen from biomass via two thermo chemical processes:

1) Gasification followed by reforming of the syngas, and 2) fast pyrolysis followed by reforming of the carbohydrate fraction of the bio-oil.

The available biomass includes sources like forestry products, agriculture byproducts, municipal and industrial solid fibrous wastes etc. Carbon dioxide from the atmosphere and water from the earth gets combined in the photosynthetic process to produce carbohydrates (sugars) that form the building blocks of biomass. The solar energy that drives photosynthesis is stored in the chemical bonds of the structural components of biomass. If we burn biomass efficiently (extract the energy stored in the chemical bonds), oxygen from the atmosphere combines with the carbon in plants to produce carbon dioxide and water. The process is cyclic because the carbon dioxide is then available to produce fresh biomass

Biomass is considered to be one of the key renewable resources of the future at both small and large-scale levels for developing countries like India. It already supplies 14 % of the world's primary energy consumption, with three quarters of the world's population living in developing countries consuming biomass as an important source of energy. For instance, biomass produces 38 % of the primary energy in developing countries (90 % in some countries). With increase in population and per capita demand and depletion of fossil-fuel resources, the demand for biomass is expected to increase rapidly. Biomass is likely to remain an important global source in developing countries well into the next century.

Hydrogen is also produced on a small scale from non-fossil energy resources by photolysis or thermolysis and gasification. As of now, there has not been any technological advancement in the production of hydrogen from biomass. Fast pyrolysis is one of the methods for the same. Fast pyrolysis is a high temperature process in which biomass is rapidly heated in the absence of oxygen. As a result, it decomposes to generate mostly vapors and aerosols and some charcoal. On cooling and condensation, a dark brown mobile liquid is formed which has a heating value about half that of conventional fuel oil. While it is related to the traditional pyrolysis processes for making charcoal, fast pyrolysis is an advanced process that is carefully controlled to give high yields of liquid and gases.

The essential conditions of a fast pyrolysis process are very high heating and heat transfer rates, which usually requires a finely ground biomass feed; carefully controlled pyrolysis reaction temperature of around 900^0C in the vapour phase, with short vapour residence times of typically less than 2 seconds; rapid cooling of the pyrolysis vapours to give the main product gases.

Country/Region	**Oil (Billion Barrels)** ***Oil & Gas Journal*** **January 1, 2006**	**Natural Gas (Trillion Cubic Feet)** ***Oil & Gas Journal*** **January 1, 2006**
Bermuda	0.000	0.000
Canada (See footnotes 2-4.)	178.792	56.577
Greenland	0.000	0.000
Mexico	12.882	15.985
Saint Pierre and Miquelon	0.000	0.000
United States (See footnotes 2-5.)	21.371	192.513
North America	**213.046**	**265.075**
Antarctica	0.000	0.000
Antigua and Barbuda	0.000	0.000
Argentina	2.320	18.866
Aruba	0.000	0.000
Bahamas, The	0.000	0.000
Barbados	0.003	0.005
Belize	0.000	0.000
Bolivia	0.441	24.000
Brazil	11.243	11.515
Cayman Islands	0.000	0.000
Chile	0.150	3.460
Colombia	1.542	4.040
Costa Rica	0.000	0.000
Cuba	0.750	2.500
Dominica	0.000	0.000
Dominican Republic	0.000	0.000
Ecuador	4.630	0.345
El Salvador	0.000	0.000
Falkland Islands	0.000	0.000
French Guiana	0.000	0.000
Grenada	0.000	0.000
Guadeloupe	0.000	0.000
Guatemala	0.526	0.109
Guyana	0.000	0.000

Haiti	0.000	0.000
Honduras	0.000	0.000
Jamaica	0.000	0.000
Martinique	0.000	0.000
Montserrat	0.000	0.000
Netherlands Antilles	0.000	0.000
Nicaragua	0.000	0.000
Panama	0.000	0.000
Paraguay	0.000	0.000
Peru	0.930	8.723
Puerto Rico	0.000	0.000
Saint Kitts and Nevis	0.000	0.000
Saint Lucia	0.000	0.000
Saint Vincent/Grenadines	0.000	0.000
Suriname	0.111	0.000
Trinidad and Tobago	0.990	25.880
Turks and Caicos Islands	0.000	0.000
Uruguay	0.000	0.000
Venezuela	79.729	151.395
Virgin Islands, U.S.	0.000	0.000
Virgin Islands, British	0.000	0.000
Other-Country Not Specified	Not Applicable	Not Applicable
Central & South America	**103.364**	**250.838**
Austria	0.062	0.530
Belgium	0.000	0.000
Bosnia and Herzegovina	0.000	0.000
Croatia	0.069	1.000
Denmark	1.328	2.786
Faroe Islands	0.000	0.000
Finland	0.000	0.000
Former Yugoslavia	Not Applicable	Not Applicable
France	0.158	0.378
Germany	0.367	9.076
Germany, East	Not Applicable	Not Applicable
Germany, West	Not Applicable	Not Applicable
Gibraltar	0.000	0.000
Greece	0.007	0.035
Iceland	0.000	0.000
Ireland	0.000	0.350
Italy	0.622	8.000
Luxembourg	0.000	0.000
Macedonia	0.000	0.000
Malta	0.000	0.000
Netherlands	0.106	62.000
Norway	7.705	84.260
Portugal	0.000	0.000
Serbia and Montenegro (Yugoslavia)	0.078	1.700

Slovenia	0.000	0.000
Spain	0.158	0.090
Sweden	0.000	0.000
Switzerland	0.000	0.000
Turkey	0.300	0.300
United Kingdom	4.029	18.750
Other-Country Not Specified	Not Applicable	Not Applicable
Western Europe	**14.989**	**189.255**
Albania	0.198	0.030
Armenia	0.000	0.000
Azerbaijan	7.000	30.000
Belarus	0.198	0.100
Bulgaria	0.015	0.210
Czech Republic	0.015	0.140
Estonia	0.000	0.000
Former Czechoslovakia	Not Applicable	Not Applicable
Former U.S.S.R.	Not Applicable	Not Applicable
Georgia	0.035	0.300
Hungary	0.102	1.210
Kazakhstan	9.000	65.000
Kyrgyzstan	0.040	0.200
Latvia	0.000	0.000
Lithuania	0.012	0.000
Moldova	0.000	0.000
Poland	0.096	5.820
Romania	0.956	3.550
Russia	60.000	1,680.000
Slovakia	0.009	0.530
Tajikistan	0.012	0.200
Turkmenistan	0.546	71.000
Ukraine	0.395	39.600
Uzbekistan	0.594	66.200
Other Former U.S.S.R.	Not Applicable	Not Applicable
Other-Country Not Specified	Not Applicable	Not Applicable
Eastern Europe & Former U.S.S.R.	**79.224**	**1,964.090**
Bahrain	0.125	3.250
Cyprus	0.000	0.000
Iran	132.460	971.150
Iraq	115.000	111.950
Israel	0.002	1.375
Jordan	0.001	0.220
Kuwait[6]	104.000	56.015
Lebanon	0.000	0.000
Oman	5.506	29.280
Qatar	15.207	910.520

Saudi Arabia[6]	266.810	241.840
Syria	2.500	8.500
United Arab Emirates	97.800	214.400
Yemen	4.000	16.900
Other-Country Not Specified	Not Applicable	Not Applicable
Middle East	**743.411**	**2,565.400**
Algeria	11.350	160.505
Angola	5.412	1.620
Benin	0.008	0.040
Botswana	0.000	0.000
Burkina Faso	0.000	0.000
Burundi	0.000	0.000
Cameroon	0.400	3.900
Cape Verde	0.000	0.000
Central African Republic	0.000	0.000
Chad	1.500	0.000
Comoros	0.000	0.000
Congo (Brazzaville)	1.506	3.200
Congo (Kinshasa)	0.187	0.035
Cote d'Ivoire (IvoryCoast)	0.100	1.000
Djibouti	0.000	0.000
Egypt	3.700	58.500
Equatorial Guinea	0.012	1.300
Eritrea	0.000	0.000
Ethiopia	0.0004	0.880
Gabon	2.499	1.200
Gambia, The	0.000	0.000
Ghana	0.017	0.840
Guinea	0.000	0.000
Guinea-Bissau	0.000	0.000
Kenya	0.000	0.000
Lesotho	0.000	0.000
Liberia	0.000	0.000
Libya	39.126	52.650
Madagascar	0.000	0.000
Malawi	0.000	0.000
Mali	0.000	0.000
Mauritania	0.000	0.000
Mauritius	0.000	0.000
Morocco	0.001	0.060
Mozambique	0.000	4.500
Namibia	0.000	2.200
Niger	0.000	0.000
Nigeria	35.876	184.660
Reunion	0.000	0.000
Rwanda	0.000	2.000
Saint Helena	0.000	0.000

Sao Tome and Principe	0.000	0.000
Senegal	0.000	0.000
Seychelles	0.000	0.000
Sierra Leone	0.000	0.000
Somalia	0.000	0.200
South Africa	0.016	0.001
Sudan	0.563	3.000
Swaziland	0.000	0.000
Tanzania	0.000	0.800
Togo	0.000	0.000
Tunisia	0.308	2.750
Uganda	0.000	0.000
Western Sahara	0.000	0.000
Zambia	0.000	0.000
Zimbabwe	0.000	0.000
Other-Country Not Specified	Not Applicable	Not Applicable
Africa	**102.580**	**485.841**
Afghanistan	0.000	1.750
American Samoa	0.000	0.000
Australia	1.437	27.640
Bangladesh	0.028	5.000
Bhutan	0.000	0.000
Brunei	1.350	13.800
Burma	0.050	10.000
Cambodia	0.000	0.000
China	18.250	53.325
Cook Islands	0.000	0.000
Fiji	0.000	0.000
French Polynesia	0.000	0.000
Guam	0.000	0.000
Hawaiian Trade Zone	Not Applicable	Not Applicable
Hong Kong	0.000	0.000
India	5.848	38.880
Indonesia	4.301	97.786
Japan	0.059	1.400
Kiribati	0.000	0.000
Korea, North	0.000	0.000
Korea, South	0.000	0.000
Laos	0.000	0.000
Macau	0.000	0.000
Malaysia	3.000	75.000
Maldives	0.000	0.000
Mongolia	0.000	0.000
Nauru	0.000	0.000
Nepal	0.000	0.000
New Caledonia	0.000	0.000
New Zealand	0.053	0.900

Niue	0.000	0.000
Pakistan	0.289	28.153
Papua New Guinea	0.240	12.200
Philippines	0.139	3.960
Samoa	0.000	0.000
Singapore	0.000	0.000
Solomon Islands	0.000	0.000
Sri Lanka	0.000	0.000
Taiwan	0.002	0.297
Thailand	0.291	14.754
Tonga	0.000	0.000
U.S. Pacific Islands	0.000	0.000
Vanuatu	0.000	0.000
Vietnam	0.600	6.800
Wake Island	0.000	0.000
Other-Country Not Specified	Not Applicable	Not Applicable
Asia & Oceania	**35.936**	**391.645**
World Total	**1,292.550**	**6,112.144**

Table 1: World proved reserves of oil and natural gas

CHAPTER 2

HYDROGEN

2.0 HYDROGEN

2.1 History of Hydrogen

Hydrogen has received increased attention, as a renewable and environmental friendly option to meet present energy requirements. The path leading to an understanding of hydrogen's energy potential presents a fascinating tour through scientific discovery and industrial ingenuity [2].

British scientist Henry Cavendish first identified in 1766, Hydrogen, as a distinct element after he evolved hydrogen gas by reacting zinc metal with hydrochloric acid. In a demonstration to the Royal Society of London, Cavendish applied spark to hydrogen gas yielding water. This discovery led to his later finding that water (H_2O) is made of hydrogen and oxygen.

In 1783, Jacques Alexander Cesar Charles, a French physicist, launched the first hydrogen balloon flight. Known as "Charliere," the unmanned balloon flew to an altitude of three kilometers. Only three months later, Charles himself flew in his first manned hydrogen balloon.

In 1788, Building on the discoveries of Cavendish, French chemist Antoine Lavoisier gave hydrogen its name, which was derived from the Greek words—"hydro" and "genes," meaning "water" and "born of."

In 1800, English scientists William Nicholson and Sir Anthony Carlisle discovered that applying electric current to water produced hydrogen and oxygen gases. This process was later termed "electrolysis."

In 1838, Swiss chemist Christian Friedrich Schoenbein discovered the fuel cell effect, combining hydrogen and oxygen gases to produce water and an electric current.

In 1845, Sir William Grove, an English scientist and judge, demonstrated Schoenbein's discovery on a practical scale by creating a "gas battery." He earned the title "Father of the Fuel Cell" for his achievement

In 1874, Jules Verne, an English author, prophetically examined the potential use of hydrogen as a fuel in his popular work of fiction entitled *The Mysterious Island.*

In 1889, Ludwig Mond and Charles Langer attempted to build the first fuel cell device using air and industrial coal gas. They named the device a fuel cell.

In 1920s German engineer, Rudolf Erren, converted the internal combustion engines of trucks, buses, and submarines to use hydrogen or hydrogen mixtures. British scientist and Marxist writer, J.B.S. Haldane, introduced the concept of renewable hydrogen in his paper Science and the Future by proposing that "there will be great power stations where during windy weather the surplus power will be used for the electrolytic decomposition of water into oxygen and hydrogen."

In 1937 after ten successful trans-Atlantic flights from Germany to the United States, the Hindenburg, a dirigible inflated with hydrogen gas, crashed upon landing in Lakewood, New Jersey. The mystery of the crash was solved in 1997. A study concluded that the explosion was not due to the hydrogen gas, but rather to a weather-related static electric discharge which ignited the airship's silver-colored, canvas exterior covering which had been treated with the key ingredients of solid rocket fuel.

In 1958, The United States formed the National Aeronautics and Space Administration (NASA). NASA's space program currently uses the most liquid hydrogen worldwide, primarily for rocket propulsion and as a fuel for fuel cells.

In 1959, Francis T. Bacon of Cambridge University in England built the first practical hydrogen-air fuel cell. The 5-kilowatt (kW) system powered a welding machine. He named his fuel cell design the "Bacon Cell." Later that year, Harry Karl Ihrig, an engineer for the Allis Chalmer's Manufacturing Company, demonstrated the first fuel cell vehicle: a 20–horsepower tractor. Hydrogen fuel cells, based upon Francis T. Beacon's design, have been used to generate on-board electricity, heat, and water for astronauts aboard the famous Apollo spacecraft and all subsequent space shuttle missions.

In 1973, The OPEC oil embargo and the resulting supply shock suggested that the era of cheap petroleum had ended and that the world needed alternative fuels. The development of hydrogen fuel cells for conventional commercial applications began.

In 1974, International Energy Agency (IEA) was established in response to global oil market disruptions. IEA activities included the research and development of hydrogen energy technologies.

In 1988, The Soviet Union Tupolev Design Bureau successfully converted a 164-passenger TU-154 commercial jet to operate one of the jet's three engines on liquid hydrogen. The maiden flight lasted 21 minutes.

In 1990, the world's first solar-powered hydrogen production plant at Solar-Wasserstoff-Bayern, a research and testing facility in southern Germany, became operational. The U.S. Congress passed the Spark M. Matsunaga Hydrogen, Research, Development and Demonstration Act (PL 101-566), which prescribed the formulation of a 5-year management and implementation plan for hydrogen research and development in the United States. The Hydrogen Technical Advisory Panel (HTAP) was mandated by the Matsunaga Act to ensure consultation on and coordination of hydrogen research. Work on a methanol-fueled 10-kilowatt (kW) Proton Exchange Membrane (PEM) fuel cell began through a partnership including GM, Los Alamos National Laboratory, the Dow Chemical Company, and Canadian fuel cell developer, Ballard Power Systems.

In 1994, Daimler Benz demonstrated its first NECAR I (New Electric CAR) fuel cell vehicle at a press conference in Ulm, Germany.

In 2003, President George W. Bush announced in his 2003 State of the Union Address a $1.2 billion hydrogen fuel initiative to develop the technology for commercially viable hydrogen-powered fuel cells, such that "the first car driven by a child born today could be powered by fuel cells."

In 2004, the world's first fuel cell-powered submarine undergoes deepwater trials (Germany navy).

In the future, renewable source will replace fossil fuels as the primary resource for hydrogen. Hydrogen will be distributed via national networks of hydrogen transport pipelines and fueling stations. Hydrogen energy and fuel cell power will be clean, abundant, reliable, affordable and an integral part of all sectors of the economy in all regions of the world.

2.2 PROPERTIES

2.2.1 Atomic structure

Hydrogen is by far the most plentiful element in the universe, making up 75% of the mass of all visible matter in stars and galaxies. Hydrogen is the simplest of all elements. One can visualize a hydrogen atom as a dense central nucleus with a single orbiting electron, much like a single planet in orbit around the sun. Scientists prefer to describe the electron as occupying a "probability cloud" that surrounds the nucleus somewhat like a fuzzy, spherical shell.

In most hydrogen atoms, the nucleus consists of a single proton, although a rare form (or "isotope") of hydrogen contains both a proton and a neutron. This form of hydrogen is called deuterium or heavy hydrogen. Other isotopes of hydrogen also exist, such as tritium with two neutrons and one proton, but these isotopes are unstable and decay radioactively.

Chemically, the atomic arrangement of a single electron orbiting a nucleus is highly reactive. For this reason, hydrogen atoms naturally combine into molecular pairs (H_2 instead of H). To further complicate things, each proton in a hydrogen pair has a field associated with it that can be visualized and described mathematically as a "spin". Molecules in which both protons have the same spin are known as "orthohydrogen". Molecules in which the protons have opposite spins are known as "Para hydrogen".

Over 75% of normal hydrogen at room temperature is ortho hydrogen. This difference becomes important at very low temperatures since orthohydrogen becomes unstable and changes to the more stable Para hydrogen arrangement, releasing heat in the process. This heat can complicate low temperature hydrogen processes, particularly liquefaction.

Hydrogen (atomic weight 1.00794amu, atomic number=1) is the first element in the periodic table having the electronic configuration $1s^1$. It has usually the oxidation state of +1 but in salt type hydrides –1 is also possible. It has three isotopes, $^1H_1$, $^2H_1$ & $^3H_1$ with half-lives stable, stable, and 12.3 years respectively. These are hydrogen, deuterium and tritium respectively.

2.2.2 Physical Properties

2.2.2.1 State

All substances exist on earth as a gas, liquid or solid. Most substances will change from one of these states to another depending on the temperature and pressure of their surroundings. In general, a gas can be changed into a liquid by reducing its temperature, and a liquid to a solid by reducing its temperature further. To some extent, an increase in pressure will cause a substance to liquefy and solidify at higher temperature than would otherwise be required. Boiling and freezing temperatures are most meaningfully compared relative to "absolute zero". Absolute zero (0°R; 0 K; –459.69°F; –273.15°C) is the lowest temperature in the universe at which all-molecular motion stops.

Hydrogen has the second lowest boiling point and melting points of all substances, second only to helium. Hydrogen is a liquid below its boiling point of -252.87°C (20.280005K, -423.166°F) and a solid below its melting point of -259.14°C (14.009985 K, -434.45203°F) and atmospheric pressure [3].

The boiling point of a fuel is a critical parameter since it defines the temperature to which it must be cooled in order to store and use it as a liquid. Liquid fuels take up less storage space than gaseous fuels, and are generally easier to transport and handle. For this reason, fuels that are liquid at atmospheric conditions (such as gasoline, diesel, methanol and ethanol) are particularly convenient. Conversely, fuels that are gases at atmospheric conditions (such as hydrogen and natural gas) are less convenient as they must be stored as a pressurized gas or as a cryogenic liquid.

The boiling point of a pure substance increases with applied pressure up to a point. Propane, with a boiling point of –44 °F (–42 °C), can be stored as a liquid under moderate pres-sure, although it is a gas at atmospheric pressure. (At temperatures of 70 °F (21 °C) a minimum pressure of 111 psig (7.7 barg) is required for liquefaction). Unfortunately, hydrogen's boiling point can only be increased to a maximum of -400 °F (–240 °C) through the application of approximately 195 psig (13 barg), beyond which additional pressure has no beneficial effect. Hydrogen as a vehicle fuel can be stored either as a high-pressure gas or as a cryogenic liquid.

2.2.2.2 Odor, Color and Taste

Pure hydrogen is odorless, colorless and tasteless. A stream of hydrogen from a leak is almost invisible in daylight. Compounds such as mercaptans and thiophanes that are used to scent natural gas may not be added to hydrogen for fuel cell use as they contain sulfur that would poison the fuel cells. Nitrogen, carbon dioxide, carbon monoxide and other trace gases typically accompany hydrogen that derives from reforming other fossil fuels. In general, all of these gases are also odorless, colorless and tasteless.

2.2.2.3 Toxicity

Hydrogen is non-toxic but can act as a simple asphyxiant by displacing the oxygen in the air.

Inhaled hydrogen can result in a flammable mixture within the body. Inhaling hydrogen can lead to unconsciousness and asphyxiation.

2.2.2.4 Density and related measures

Hydrogen has lowest atomic weight of any substance and therefore has very low density both as a gas and a liquid [3].

Substance	**Vapor density (At 68^{0}F, 1atm)**	**Liquid density** *(At normal boiling point, 1atm)*
Hydrogen	0.005229 lb/ft3 (0.08376 kg/m3)	4.432 lb/ft3 (70.8 kg/m3)
Methane	0.0406 lb/ft3 (0.65 kg/m3)	26.4 lb/ft3 (422.8 kg/m3)
Gasoline	0.275 lb/ft3 (4.4 kg/m3)	43.7 lb/ft3 (700 kg/m3)

Table 2: Vapor and Liquid Densities of Comparative Substances

Specific Volume

Specific volume is the inverse of density and expresses the amount of volume per unit mass. Thus, the specific volume of hydrogen gas is 191.3 ft3/lb (11.9 m3/kg) at 68 °F (20 °C) and 1 atm, and the specific volume of liquid hydrogen is 0.226 ft3/lb (0.014 m3/kg) at –423 °F (–253 °C) and 1 atm.

Specific gravity

Gaseous hydrogen, with a density of 0.00523 lb/ft3, has a specific gravity of 0.0696 and is thus approximately 7% the density of air.

Liquid hydrogen, with a density of 4.432 lb/ft3, has a specific gravity of 0.0708 and is thus approximately (and coincidentally) 7% the density of water.

•

Expansion Ratio

The difference in volume between liquid and gaseous hydrogen can easily be appreciated by considering its expansion ratio. Expansion ratio is the ratio of the volume at which a gas or liquid is stored compared to the volume of the gas or liquid at atmospheric pressure and temperature.

When hydrogen is stored as a liquid, is vaporizes upon expansion to atmospheric conditions with a corresponding increase in volume. Hydrogen's expansion ratio of 1:848 means that hydrogen in its gaseous state at atmospheric conditions occupies 848 times more volume than it does in its liquid state.

When hydrogen is stored as a high-pressure gas at 3600 psig (250 barg) and atmospheric temperature, its expansion ratio to atmospheric pressure is 1:240. While a higher storage pressure increases the expansion ratio somewhat, gaseous hydrogen under any conditions cannot approach the expansion ratio of liquid hydrogen.

When used as vehicle fuel, the low density of hydrogen necessitates that a large volume of hydrogen be carried to provide an adequate driving range.

2.2.2.5 ***Leakage***

The molecules of hydrogen gas are smaller than all other gases, and it can diffuse through many materials considered airtight or impermeable to other gases. This property makes hydrogen more difficult to contain than other gases. Leaks of liquid hydrogen evaporate very quickly since the boiling point of liquid hydrogen is so extremely low.

For small hydrogen leaks, buoyancy and diffusion effects in air are often overshadowed by the presence of air currents from a slight ambient wind, very slow vehicle motion or the radiator fan. In general, these currents serve to disperse leaked hydrogen even more quickly with a further reduction of any associated fire hazard.

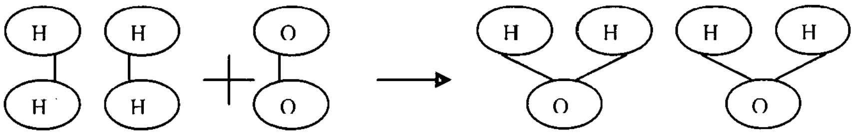
When used as vehicle fuel, the propensity for hydrogen to leak necessitates special care in the design of the fuel system to ensure that any leaks can disperse with minimum Hindrance and the use of dedicated leak detection equipment on the vehicle and within the maintenance facility.

2.2.3 Chemical Properties

2.2.3.1 Reactivity

High reactivity is characteristic of all chemical fuels. In each case, a chemical reaction occurs when the fuel molecules form bonds with oxygen (from air) so that the final, reacted molecules are at a lower energy state than the initial, unreacted molecules.

$2H_2 + O_2 \longrightarrow$



High-energy state Reaction Energy released Low energy state

Chemical reactions of this type often require a small amount of activation energy to get started, but then the energy re-leased by the reaction feeds further reaction in a domino effect. Thus, when a small amount of activation energy in the form of a spark is provided to a mixture of hydrogen and oxygen, the molecules react vigorously, releasing a substantial amount of heat, with water as the final product. We experience this reaction as a fire or explosion, and the resulting water vaporizes and is invisible to us since it is a superheated vapor. (This water vapor can condense and become visible as it cools; this is the cloud we see when the space shuttle takes off.)

2.2.3.2 Energy content

Every fuel can liberate a fixed amount of energy when it reacts completely with oxygen to form water. This energy content is measured experimentally and is quantified by a Fuels' higher heating value (HHV) and lower heating value (LHV). The difference between the HHV and the LHV is the "heat of vaporization" and represents the amount of energy required to vaporize a liquid fuel into a gaseous fuel, as well as the energy used to content is measured experimentally and is quantified by a fuel's higher heating value (HHV) and lower heating value (LHV).

The difference between the HHV and the LHV is the "heat of vaporization" and represents the amount of energy required to vaporize a liquid fuel into a gaseous fuel, as well as the energy used to convert water to steam.

The higher and lower heating values of comparative fuels are indicated in Table 1-3.

Fuel	**Higher heating value (At 25^{0}c and 1atm)**	**Lower heating value (At 25^{0}c and 1atm)**
Hydrogen	61,000 Btu/lb (141.86 kJ/g)	51,500 Btu/lb (119.93 kJ/g)
Methane	24,000 Btu/lb (55.53 kJ/g)	21,500 Btu/lb (50.02 kJ/g)
Propane	21,650 Btu/lb (50.36 kJ/g)	19,600 Btu/lb (45.6 kJ/g)
Gasoline	20,360 Btu/lb (47.5 kJ/g)	19,000 Btu/lb (44.5 kJ/g)
Diesel	19,240 Btu/lb (44.8 kJ/g)	18,250 Btu/lb (42.5 kJ/g)
Methanol	8,580 Btu/lb (19.96 kJ/g)	7,760 Btu/lb (18.05 kJ/g)

Table 3: Heating Values of Comparative Fuels

Specifically, the amount of energy liberated during the reaction of hydrogen, on a mass basis, is about 2.5 times the heat of combustion of common hydrocarbon fuels (gasoline, Diesel, methane, propane, etc.) Therefore, for a given load duty, the mass of hydrogen required is only about a third of the mass of hydrocarbon fuel needed.

The high-energy content of hydrogen also implies that the energy of a hydrogen gas explosion is about 2.5 times that of common hydrocarbon fuels. Thus, on an equal mass basis, hydrogen gas explosions are more destructive and carry further. However, the duration of a conflagration tends to be inversely proportional to the combustive energy, so that hydrogen fires subside much more quickly than hydrocarbon fires.

2.2.3.3 Energy Density

Whereas the energy content denotes the amount of energy for a given weight of fuel, the energy density denotes the amount of energy (in Btu's or Joules) for a given volume (in ft^3 or m^3) of fuel. Thus, energy density is the product of the energy content (LHV in our case) and the density of a given fuel.

Fuel	**Energy Density (LHV)**
Hydrogen	270 Btu/ft$_3$ (10,050 kJ/m$_3$); gas at 1 atm and 60 °F (15 °C) 48,900 Btu/ft$_3$ (1,825,000 kJ/m$_3$); gas at 3,000 psig (200 barg) and 60 °F (15 °C) 121,000 Btu/ft$_3$ (4,500,000 kJ/m$_3$); gas at 10,000 psig (690 barg) and 60 °F (15 °C) 227,850 Btu/ft$_3$ (8,491,000 kJ/m$_3$); liquid
Methane	875 Btu/ft$_3$ (32,560 kJ/m$_3$); gas at 1 atm and 60 °F (15 °C) 184,100 Btu/ft$_3$ (6,860,300 kJ/m$_3$); gas at 3,000 psig (200 barg) and 60 °F (15 °C) 561,500 Btu/ft$_3$ (20,920,400 kJ/m$_3$); liquid
Propane	2,325 Btu/ft$_3$ (86,670 kJ/m$_3$); gas at 1 atm and 60 °F (15 °C) 630,400 Btu/ft$_3$ (23,488,800 kJ/m$_3$); liquid
Gasoline	836,000 Btu/ft$_3$ (31,150,000 kJ/m$_3$); liquid
Diesel	843,700 Btu/ft$_3$ (31,435,800 kJ/m$_3$) minimum; liquid
Methanol	424,100 Btu/ft$_3$ (15,800,100 kJ/m$_3$); liquid

Table 4: Energy Densities of Comparative Fuels

The energy density of a fuel is also affected by whether the fuel is stored as a liquid or as a gas, and if a gas, at what pressure. To put it into perspective:

- A 132-gal (500-L) diesel tank containing 880 lb (400 kg) of fuel is equivalent on an energy basis to a 2110 gal (8000 L) volume of hydrogen gas at 3600 psi (250 barg). This is a 16 times increase in volume, although the weight of the hydrogen is only 330 lb (150 kg), representing a decrease in fuel weight by a factor of about 2.8.
- The same diesel tank is equivalent to a 550-gal (2100-L) tank of liquid hydrogen. This is a 4.2 times increase in volume.
- If hydrogen is stored as a metal hydride, every kilogram of diesel fuel is replaced by approximately 4.5 kg of metal hydride to maintain the same hydrogen/diesel energy equivalence. Thus the same 132 gal (500 L) diesel tank containing 880 lb (400 kg) of fuel would have to be re-placed with a hydride tank containing 3800 lb (1725 kg) of "fuel" mass.

2.2.3.4 Flammability

Three things are needed for a fire or explosion to occur: a fuel, oxygen (mixed with the fuel in appropriate quantities) and a source of ignition. Hydrogen, as a flammable fuel, mixes with oxygen whenever air is allowed to enter a hydrogen vessel, or when hydrogen leaks from any vessel into the air. Ignition sources take the form of sparks, flames, or high heat.

Flashpoint

All fuels burn only in a gaseous or vapor state. Fuels like hydrogen and methane are already gases at atmospheric conditions, whereas other fuels like gasoline or diesel that are liquids must convert to a vapor before they will burn. The characteristic that describes how easily these fuels can be converted to a vapor is the flashpoint. The flashpoint is defined as the temperature at which the fuel produces enough vapors to form an ignitable mixture with air at its surface.

If the temperature of the fuel is below its flashpoint, it cannot produce enough vapors to burn since its evaporation rate is too slow. Whenever a fuel is at or above its flashpoint, vapors are present. The flashpoint is not the temperature at which the fuel bursts into flames; that is the auto ignition temperature.

The flashpoint is always lower than the boiling point. For fuels that are gases at atmospheric conditions the flashpoint is far below ambient temperature and has little relevance since the fuel is already fully vaporized. For fuels that are liquids at atmospheric conditions, the flash point acts as a lower flammability temperature limit.

Fuel	Flash point
Hydrogen	< –423 °F (< –253 °C; 20 K)
Methane	–306 °F (–188 °C; 85 K)
Propane	–156 °F (–104 °C; 169 K)
Gasoline	Approx –45 °F (–43 °C; 230 K)
Methanol	52 °F (11 °C; 284 K)

Table 5: Flashpoint of Comparative Fuels

Flammability Range

The flammability range of a gas is defined in terms of its lower flammability limit (LFL) and its upper flammability limit (UFL). The LFL of a gas is the lowest gas concentration that will support a self-propagating flame when mixed with air and ignited. Below the LFL, there is not enough fuel present to support combustion; the fuel/air mixture is too lean.

The UFL of a gas is the highest gas concentration that will support a self-propagating flame when mixed with air and ignited. Above the UFL, there is not enough oxygen present to support combustion; the fuel/air mixture is too rich. Between the two limits is the flammable range in which the gas and air are in the right proportions to burn when ignited. One consequence of the UFL is that stored hydrogen (whether gaseous or liquid) is not flammable while stored due to the absence of oxygen in the cylinders. The fuel only becomes flammable in the peripheral areas of a leak where the fuel mixes with the air in sufficient proportions.

An explosion is different from a fire in that for an explosion; the combustion must be contained, allowing the pressure and temperature to rise to levels sufficient to violently destroy the containment. For this reason, it is far more dangerous to release hydrogen into an enclosed area (such as a building) than to release it directly outdoors.

Hydrogen is flammable over a very wide range of concentrations in air (4 – 75%) and it is explosive over a wide range of concentrations (15 – 59%) at standard atmospheric temperature. The flammability limits increase with temperature as illustrated in Figure 1. As a result, even small leaks of hydrogen have the potential to burn or explode. Leaked hydrogen can concentrate in an enclosed environment, thereby increasing the risk of combustion and explosion. The flammability limits of comparative fuels are illustrated in Table 7.

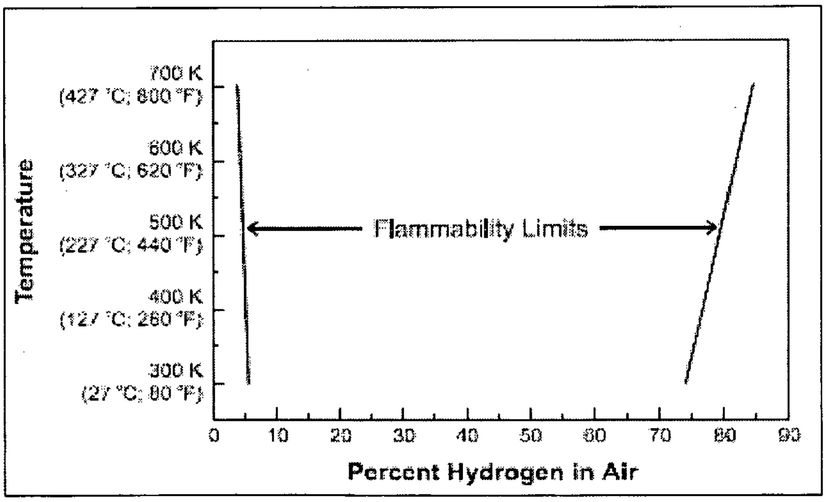


Figure 1: Variations of Hydrogen Flammability Limits with Temperature

Fuel	Flammable Range at atm Temparature
Hydrogen	4% to 75%
Methane	5.2% to 15%
Propane	2.25 to 9.6%
Methanol	6.0% to 36.5%
Gasoline	1.0% to 7.6%
Deisel	0.6% to 5.5%

Table 6: Flammability Ranges of Comparative Fuels at Atmospheric Temperature

Auto-ignition Temperature

The auto-ignition temperature is the minimum temperature required to initiate self-sustained combustion in a combustible fuel mixture in the absence of a source of ignition. In other words, the fuel is heated until it bursts into flame.

Each fuel has a unique ignition temperature. For hydrogen, the auto-ignition temperature is relatively high at 1085 °F (585 °C). This makes it difficult to ignite a hydrogen/air mixture on the basis of heat alone without some additional ignition source. The auto-ignition temperatures of comparative fuels are indicated in Table 1-6.

Fuel	Auto-ignition temperature
Hydrogen	1085 °F (585 °C)
Methane	1003 °F (540 °C)
Propane	914 °F (490 °C)
Methanol	725 °F (385 °C)
Gasoline	450 to 900 °F (230 to 480 °C)

Table 7: Auto-ignition Temperature of Comparative Fuels

Octane number

The octane number describes the anti-knock properties of a fuel when used in an internal combustion engine. Knock is a secondary detonation that occurs after fuel ignition due to heat buildup in some other part of the combustion chamber. When the local temperature exceeds the auto-ignition temperature, knock occurs.

The performance of the hydrocarbon octane is used as a standard to measure resistance to knock, and is assigned a relative octane rating of 100. Fuels with an octane number over 100 have more resistance to auto-ignition than octane itself. Hydrogen has a very high research octane number and is therefore resistant to knock even when combusted under very lean conditions. The octane number of comparative fuels are indicated in Table 1-7. The octane number has no specific relevance for use with fuel cell.

Fuel	**Octane number**
Hydrogen	130+
Methane	125
Propane	105
Methanol	100
Gasoline	87
Diesel	30

Table 8: Octane Numbers of Comparative Fuels

Ignition Energy

Ignition energy is the amount of external energy that must be applied in order to ignite a combustible fuel mixture. Energy from an external source must be higher than the auto-ignition temperature and be of sufficient duration to heat the fuel vapor to its ignition temperature. Common ignition sources are flames and sparks.

Although hydrogen has a higher auto-ignition temperature than methane, propane or gasoline, its ignition energy at 1.9 x 10–8 Btu (0.02 mJ) is about an order of magnitude lower and is therefore more easily ignitable. Even an invisible spark or static electricity discharge from a human body (in dry conditions) may have enough energy to cause ignition.

Hydrogen has the added property of low electro-conductivity so that the flow or agitation of hydrogen gas or liquid may generate electrostatic charges that result in sparks. For this reason, all hydrogen conveying equipment must be thoroughly grounded.

Burning Speed

The burning speed of hydrogen at 8.7–10.7 ft/s (2.65–3.25 m/s) is nearly an order of magnitude higher than that of methane or gasoline (at stoichiometric conditions). Thus hydrogen fires burn quickly and, as a result, tend to be relatively short-lived.

Quenching Gap

The quenching gap (or quenching distance) describes the flame extinguishing properties of a fuel when used in an internal combustion engine. Specifically, the quenching gap relates to the distance from the cylinder wall that the flame extinguishes due to heat losses. The quenching gap has no specific relevance for use with fuel cells. The quenching gap of hydrogen (at 0.025 in; 0.064 cm) is approximately 3 times less than that of other fuels.

Flame Characteristics

Hydrogen flames are very pale blue and are almost invisible in daylight due to the absence of soot. Visibility is enhanced by the presence of moisture or impurities (such as sulfur) in the air. Hydrogen flames are readily visible in the dark or subdued light.

A hydrogen fire can be indirectly visible by way of emanating “heat ripples” and thermal radiation, particularly from large fires. In many instances, flames from a hydrogen fire may ignite surrounding materials that do pro-duce smoke and soot during combustion.

Hydrogen burns with greater vigor than gasoline, but for a shorter time. Pools of liquid hydrogen burn very rapidly at 0.098 to 0.197 ft/min (3 to 6 cm/min) compared to 0.0098 to 0.00656 ft/min (0.3 to 1.2 cm/min) for liquid methane, and 0.00656 to 0.0295 ft/min (0.2 to 0.9 cm/min) for gasoline pools.

2.2.3.5 Hydrogen Embrittlement

Constant exposure to hydrogen causes a phenomenon known as hydrogen embrittlement in many materials. Hydrogen embrittlement can lead to leakage or catastrophic failure, in metal and non-metallic components.

The mechanisms that cause hydrogen embrittlement effects are not well defined. Factors known to influence the rate and severity of hydrogen embrittlement include hydrogen concentration, hydrogen pressure, and temperature, and hydrogen purity, type of impurity, stress level, stress rate, metal composition, metal tensile strength, grain size, microstructure and heat treatment history. Moisture content in the hydrogen gas may lead to metal embrittlement through the acceleration of the formation of fatigue cracks.

2.3. Path-ways of Hydrogen production

Hydrogen can be produced from a wide range of source materials. Some of the methods & sources by which H_2 is produced till date are as follows.

2.3.1 Natural gas:

Natural gas is the cleanest of all fossil fuels and has highest H/C ratio, as it is almost fully methane. Hydrogen from natural gas for the ammonia and petroleum industries includes the larges portion of the current global production market.

H_2 can be produced from natural gas directly via processes including steam reforming, partial oxidation, auto thermal reforming and thermal decomposition. [3]

2.3.2 Oil/Petroleum

Hydrogen can be produced from oil/petroleum. But due to scarcity of these, there is not much time left for unavailability of H_2 from oil/petroleum. [3]

2.3.3 Coal

Hydrogen can be produced from coal by two main processes – gasification and by use of coal to generate electricity to electrolyze water. Out of the two-gasification process are more environments friendly.

Coal has the lowest H/C ratio; so more CO_2 is produced per mole of H_2. H_2 production from coal conversion under high power electric beams has been studied with an 80 KW beam. Product formation rates, energy consumption and energy storage in products were determined and a comparison between traditional coal conversion methods was made. Soo et. at. (1978)(USA) present calculations and experimental data on steam processes to convert coal to hydrogen. A large excess of steam (4moles water to 1 mole carbon) at 130^0 C produce up to90% hydrogen with out the need for shift conversion. It was claimed that their processes are better source of hydrogen than Hygas or steam iron. [41].

Williams (1980) (USA) makes a case for efficient hydrogen production from coal using centrifuge separation of hydrogen from other gases following steam gasification at 110^0-500^0C.

U-gas process:

The U- gas process for producing hydrogen from coal is discussed by Dihu and Patel (1983) (USA). U-Gas has been developed by IGT from over fifty years of coal-conversion research. It comprises a single stage, non-slogging, fluidized bed gasifier using oxygen or air. [41]

Hydrogen production from coal conversion under high power electric beams has been studied with an 80KW beam.

Yermakov et.al. (Russia) (1944) discussed the preliminary results for coal using an election accelerator as a radiation source.

2.3.4 Water:

Electrolysis of water produces high purity H_2 with high efficiency. The electrical energy required may be produced by a wide variety of methods, and it is this electricity source that is the strongest determining factor in the environmental benefit of using this process. A total of ca 5% of the world H_2 production is by means of electrolysis. The following runs take place. [3]

Cathode: $2H_2O(I) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

Anode: $2OH^-(aq) \rightarrow \frac{1}{2} O_2(g) + H_2O(l) + 2e^-$

Thakur (1980) (India) tested the production of hydrogen by the electrolysis of a mixture of coal water and lime.

2.3.5 Chemical

Various chemical sources mainly by products of industrial processes or impurities in other fuel sources exist for the production of H_2. H_2S is one source, which is formed as by product during H_2 reduction of sulphides. This H_2S can be broken down to H_2 & S by electrolytic & Photo catalytic processes. [3]

2.3.6 H_2 from Ammonia

Ammonia is easily thermally decompose via $2NH_3 \rightarrow N_2 + 3H_2$ $\Delta H_{298} =+ 91.86$ KJ/mol reaction. From 1 kg of ammonia 1-07m^3 (STP) of H_2 and 0.66m^3 of N_2 are obtained.

2.3.7 Biological H_2 Production

Many phototropic organisms such as purple bacteria, green bacteria, cyno bacteria, and several algae on produce hydrogen with the aid of solar energy. The mechanism varies from organism to organism. The main steps, however, are similar to those of photosynthesis shown below [43]:

PC – Plastocyanins [Mn} = Manganese
Fd = Ferredoxin
PSI & PSII - Photo systems I & II
Y, X = Primary CH acceptors of PSI & PSII
Chl – Chlorophyll
Q = Plastoquinone
Cyt B, Cyt C = Cytochrome B & Cytochrome C

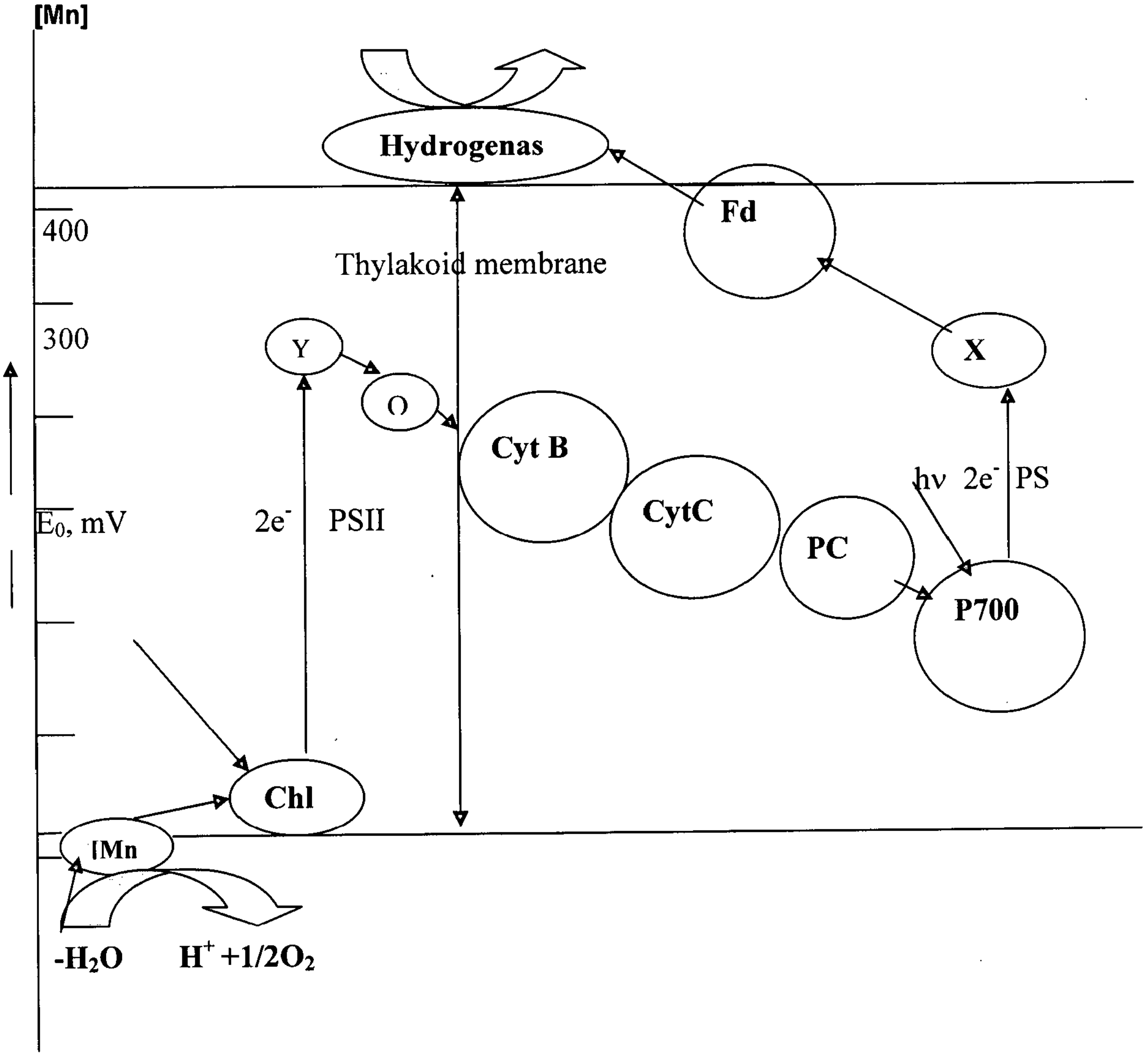


Fig 2: Biological H_2 Production

Some strains like Rhodopseudomonas *capsulata* produce H_2 during irradiation in presence of organic compounds such as maleate, succinate etc. Cyanobacteria (B. G. algae) represent the must numerous groups of phototropic procaryorites that can produce H_2. Table 8 shows H_2 production by some bacteria.

Phototropic microorganisms	**H evolution per hour and gram dry biomass**		
	ML	mmol	
Purple bacteria			
Rhodospirillum rubrum	146	6.5	
Rhodopseudomonas palustris A	54	2.4	
Rh. Capsulata SL	130-150	5.8-6.7	
Rh. Capsulata B 10	300-500	13.4	
Rh. Capsulata L B 2	178	7.9	
Thiocapsa roseopersicina	13	0.6	
Cyanobacteria			
Anabaena cylindrica B 629	5-40	0.2-2.0	
An.variabilis	32	1.3	
Spirulina platensis	9	0.4	
Green algae			
Chlorella vulgaris	4	0.2	
Chlamydomonas reinhardii 137 C	45	2.0	
Chl. Moevussii ICC 97	8	0.4	
Cell free systems	H evolution per hour and gram dry biomass		
	mL	mol	Fn.time,h
Chp+Fd+H_2-ase (C pasteur)	200-300	9.0-15.5	3.0-6.0
Chp+Fd+H_2-ase (*Th. Roseopersicina)*	110-220	5.0-10	3.0-6.0
Chp+Fd+H_2-ase (*from various sources)*	450-900	20-40	4.0

Table 9: Hydrogen production by some bacteria

2.3.8 Hydrogen from metals

Alkali and alkaline earth metals react with water or steam (via equations below) to yield H_2. Still this is used for the production of H_2 in laboratory scale.

$$Me + H_2O \rightarrow \frac{1}{2} H_2 + MeOH$$

$$Zn + 2HCl \rightarrow H_2 + ZnCl_2$$

$$Al + NaOH + 2H_2O \rightarrow 3/2\ H_2 + NaAlO(OH)_2$$

H_2 can be obtained from metal Hydrides by heating them as well as by subject in them to the influence of water.

2.3.9 H_2 from methanol

H_2 and CO can be obtained from the decomposition of methanol by reversal of the synthesis reaction. Higher H_2 yields are obtained from catalytic steam reforming of methanol. [41]

$$CH_3OH \rightarrow CO + 2H_2 \qquad \Delta H_{298} = +91.7 \text{ KJ/mol}$$

$$CO + H2O \rightarrow CO_2 + 3H_2 \qquad \Delta H_{298} = -41.0 \text{ KJ/mol}$$

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \qquad \Delta H_{298} = +50.7 \text{ KJ/mol}$$

2.3.10 H_2 from ethanol

Ethanol likely to produce from lignocelluloses in the future, has been considered by researchers in a number of countries for hydrogen production. The advantages of both ethanol and methanol in ease of steam reforming to hydrogen via a via methane are stressed, as is the storage aspect of liquids for the vehicle and fuel cell applications [41]

Garcia and aborte (1991) (Switzerland) provides some catalysts consisting of Cu, Co,& Ni acting as basic high area supports like MgO. Another catalyst used was $CuO/ZnO/Al_2O_3$ by Cavallaro and Freni in 1996, 1998 (Italy). The process was found feasible at 800 and 1000K and pressure up to 100 bars. Some other catalysts used up to 630K are $CaO/ZnO/Al_2O_3$ and $NiO/CuO/SiO_2$. Later steam reforming on Rh/Al_2O_3 catalyst was explored.

Plasma reduction cracking of ethanol

Toci and Modica (1996) (Italy and Sweden) describe an innovative process for H_2 production by plasma reaction cracking of vaporized ethanol solution in the presence of a Ni based catalyst .The approach is the cold plasma chemical processing developed at Stuggrt University.

2.3.11 H_2 from H_2S

A potential source of H_2 is H_2S, which can be obtained, in large amounts from scrubbing processes.

$$2H_2S \rightarrow 2H_2 + \tfrac{1}{4} S_8, \qquad \Delta H_{298} = 84.90 \text{ KJ/mol}$$

2.3.12 Solar photo production of H_2:

The photo production of hydrogen was done by the decomposition of water using solar energy as a driving source. Fujishima and Honde reported the production of H_2 and O_2 in a photo electrochemical cell using titanium dioxide electrode illuminated with near UV light [29].

2.3.13 H_2 from biomass

The details are given in chapter 3.

2.4 Uses of Hydrogen:

- Used in industries as chemical feedstock for production of certain chemicals.
- Used in three main industries ammonia manufacture, petroleum refining and petrochemicals and methanol production.
- Used for hydrogenation of unsaturated oils of soybeans, fish, cottonseed, corn, peanut and coconut.
- Hydrogenation of inedible oils & greases to produce soaps and animal feed.
- Used in the production of float glass.
- Used in oxy-hydrogen cutting of glass.
- Energy storage Technology
- Liquid H_2 is stored as energy carriers
- Used in electronics industry
- Highly pure H_2 used for the production & processing of silicon.
- Hydrogen is used as an alloying element in various amorphous materials (e.g. a-Si:H, a Ge:H, a C:H and a Si C:H)

- Hydrogen used as fuel for rocket propulsion
- Used in fuel cells
- Used for the transportation

2.5 H2 as "Automotive Fuel"

The possibility of using H_2 as automotive fuel has received attention because of the increased importance of reducing exhaust emissions. When an IC engine uses pure H_2, the equivalence ratio can be extended to very low values, where exhaust emissions are reduced by several orders of magnitude. Another advantage of hydrogen engine is that it does not generate CO_2, CO, hydrocarbons, lead or S pollutants. Also using gaseous hydrogen, overcomes the problems of fuel atomization and vaporization. With air engine produces NOx. Formation of NOx can be controlled in hydrogen engines by running it very lean, thus lowering the temperature and lowering the engine rpm allowing better heat dissipation. H_2 can be considered more thermally efficient than gasoline as it burns better in excess air. On average H_2 vehicles are 22% more efficient.

CHAPER 3

BIOMASS

3.0 Biomass

3.1 History

Biomass is the fourth largest source of energy in the world, accounting for about 15% of the world's primary energy consumption and about 38% of the primary energy consumption in developing countries [35]. Biomass ranges from all the materials obtained form plants and plant sources including crops, trees, land and water flora and fauna, forestry products, agricultural by products, municipal and industrial solid fibrous wastes, animal wastes, wastes from food processing and aquatic plants and algae etc.

Simply defined, biomass is all plant material, or vegetation, raw or processed, wild or cultivated. Examples of this energy source include:

Fast growing trees and grasses, agricultural residues like used vegetable oils, wheat straw, or corn, wood waste like paper trash, yard clippings, sawdust, or wood chips, methane that is captured from landfills, livestock, and municipal waste water treatment.

Essentially, biomass is stored solar energy that man can convert to electricity, fuel, and heat. Through photosynthesis the energy from the sun is stored in the chemical bonds of the plant material. Typically biomass energy comes from three sources: agricultural crop residues, municipal and industrial waste, and energy plantations.

In addition, crops such as corn, sugar beets, grains, and kelp can be grown specifically for energy generation. Crops that make good energy resources have a high yield of dry material and use minimal land; the crop should also generate more energy than its production consumes. Numerous processes such as cogeneration, gasification, and fermentation, can tap into this energy source to produce energy available for human consumption.

3.2 Chemical composition of biomass

The chemical composition of biomass varies among species, but a plant consists of about 25% lignin and 75% carbohydrates or sugars. The carbohydrate fraction consists of many sugar molecules linked together in long chains or polymers. Two larger carbohydrate categories that have significant value are cellulose and hemi-cellulose.

The lignin fraction consists of non-sugar type molecules. Nature uses the long cellulose polymers to build the fibers that give a plant its strength. The lignin fraction acts like a "glue" that holds the cellulose fibers together.

3.3 Resources of Biomass

Carbon dioxide from the atmosphere and water from the earth are combined in the photosynthetic process to produce carbohydrates (sugars) that form the building blocks of biomass. The solar energy that drives photosynthesis is stored in the chemical bonds of the structural components of biomass. If we burn biomass efficiently (extract the energy stored in the chemical bonds) oxygen from the atmosphere combines with the carbon in plants to produce carbon dioxide and water. The process is cyclic because the carbon dioxide is again available to produce new biomass.

Wood may be the best-known example of biomass. When burnt, the wood releases the energy the tree captured from the sun's rays. But wood is just one example of biomass.

Various biomass resources such as agricultural residues (e.g. bagasse from sugarcane, corn fiber, rice straw and hulls, and nutshells), wood waste (e.g. sawdust, timber slash, and mill scrap), the paper trash and urban yard clippings in municipal waste, energy crops (fast growing trees like poplars, willows, and grasses like switch grass or elephant grass), and the methane captured from landfills, municipal waste water treatment, and manure from cattle or poultry, can also be used.

Biomass is considered to be one of the key renewable resources of the future at both small- and large-scale levels. It already supplies 14 % of the world's primary energy consumption. But for three quarters of the world's population living in developing countries biomass is the most important source of energy.

With increases in population and per capita demand, and depletion of fossil-fuel resources, the demand for biomass is expected to increase rapidly in developing countries. On average, biomass produces 38 % of the primary energy in developing countries (90% in some countries). Biomass is likely to remain an important global source in developing countries well into the next century.

BIOMASS - SOME BASIC DATA

- Total mass of living matter (including moisture) - 2000 billion tons.
- Total mass in land plants - 1800 billion tons.
- Total mass in forests -1600 billion tons
- Per capita terrestrial biomass - 400 tons.
- Energy stored in terrestrial biomass 25 000 EJ.
- Net annual production of terrestrial biomass - 400 000 million tons.
- Rate of energy storage by land biomass - 3000 EJ/y (95 TW).
- Total consumption of all forms of energy - 400 EJ/y (12 TW).
- Biomass energy consumption - 55 EJ/y (1. 7 TW).

3.4 Biomass Types

There are four main types of biomass [2]:

- Woody plants
- Herbaceous plants/ grasses
- Aquatic plants
- Manures

Among these herbaceous plants can be further subscribed into those with high and low subdivided into those with high and low moisture contents. Most commercial activities are directed towards the low moisture content plants.

3.5 Biomass in Developing countries

Despite its wide use in developing countries, biomass energy is usually used so inefficiently that only a small percentage of its useful energy is obtained. The overall efficiency in traditional use is only about 5-15 per cent, and biomass is often less convenient to use compared with fossil fuels. It can also be a health hazard in some circumstances, for example, cooking stoves can release particulates, CO, NOx formaldehyde, and other organic compounds in poorly ventilated homes, often far exceeding recommended WHO levels.

Furthermore, the traditional uses of biomass, i.e., burning of wood are often associated with the increasing scarcity of hand-gathered wood, nutrient depletion, and the problems of deforestation and desertification. In the early 1980s, almost 1.3 billion people met their fuel wood needs by depleting wood reserves.

Nepal	Malawi	Kenya	India	Brazil	Egypt	China
95%	94%	75%	50%	25%	20%	33%

Table 10: Share of biomass on total energy consumption

3.6 Biomass Properties

It is the inherent properties of any biomass source that determine both the choice of conversion process and any subsequent processing difficulties that may arise.

The main material properties of interest are [4]:

- Moisture content
- Calorific value
- Proportions of fixed carbons & volatiles
- Ash/Residue content
- Alkali metal content
- Cellulose/ lignin ratio

For dry biomass conversion processes, the first few properties are of interest, while for wet biomass conversion processes, the last few properties are of prime concern.

3.6.1 Moisture content:

Two forms of moisture content are of interest in biomass [2]:

- Intrinsic moisture
- Extrinsic moisture

In practical terms, it is the extrinsic moisture content that is of concern. Conversion to alcohol or gas/oil, the relationship between biomass moisture content and appropriate bioconversion technology is essentially straight forward, in that thermal conversion requires low moisture content feedstock while bioconversion can utilize high moisture content feedstock. On this basis, woody and low moisture content herbaceous plant species are the most efficient biomass sources for thermal conversion.

Biomass	Moisture %	Volatile Matters %	Fixed Carbon %	Ash %	LHV (MJ/kg)
Wood	20	82	17	1	18.6
Wheat straw	16	59	21	4	17.3
Barley straw	30	46	18	6	16.1
Lignite	24	29	31	6	26.8
Bituminous Coal	11	35	45	9	34.0

Table 11: shows typical moisture content of some biomass materials.

3.6.2 Calorific value:

The calorific value (CV) of a material is an expression of the energy content or heat value, released when burnt in air. It is measured as energy content per unit mass or volume, hence MJ/Kg for solids & MJ/l for liquids for MJ/NM^3 for gases. The CV of a fuel can be expressed in two forms, the gross CV (GCV), or higher heating value (HHV) and the net CV (NCV), or lower heating value (LHV). [2]

The HHV is the total energy content released when the fuel is burnt in air, including the latent heat contained in the water vapor and therefore represents the maximum amount of energy potentially recoverable from a given biomass resource. Table 10 above lists CV of a range of biomass materials.

3.6.3 Proportions of fixed carbon & volatile matter:

Fuel analysis has been developed based on solid fuels such as coal, which consists of chemical energy stored in two forms fixed C and volatiles. The volatiles content or volatile matter (VM) of a solid fuel, is that position drive off as a gas by heating. The fixed carbon content (FC) is the mass remaining after the releases of volatiles, excluding the ash and moisture content.

Fuel analysis based upon the VM content, ash and moisture with the FC determined by difference is called the proximate analysis of a fuel. Table 3.1 gives the proximate analysis of some biomass materials.

VM & FCC contents gives the measure of the ease with which the biomass can be ignited and subsequently gasified or oxidized depending on how the biomass is to be utilized as an energy source. It is useful for biological conversion [2].

3.6.7 Ash/ residue content

The solid residue produced by biomass on combustion in air is called ash. The ash content of biomass affects both the handling and processing costs of the overall, biomass energy conversion cost. [2]

For a biochemical conversion process, the solid residue represents the quantity of non-biodegradable carbon present in the biomass.

In a thermo chemical conversion process, the chemical composition of the ash can present significant operational problems. During combustion process, the ash can react to form a 'slag' a liquid phase product that can reduce the plant throughput & results in increased operational cost.

3.6.8 Alkali metal content

The alkali metal content of biomass i.e. Na, K, Mg, P & Ca is especially important for any thermo-chemical conversion processes. The reaction of alkali metals with silica present in the ash produces a sticky, mobile liquid phase, which can lead to blockages of airways in the furnace & boiler plant [2].

This is important only in biochemical conversion processes. The biodegradability of cellulose is greater than that of lignin, hence the overall conversion of the carbon containing plant material present as cellulose is greater that for plants with a higher proportion of lignin, a determining factor when selecting biomass plant species for biochemical processing. Table 11 gives the proportion of cellulose/ hemi-cellulose/ lignin in different biomass materials. [2]

Biomass	Lignin %	Cellulose %	Hemi-cellulose (%)
Softwood	27-30	35-40	25-30
Hardwood	20-25	45-50	20-25
Wheat straw	15-20	33-40	20-25
Switch grass	5-20	30-50	10-40

Table 12: The proportion of cellulose/ hemi-cellulose/ lignin in different biomass materials.

3.6.9 Bulk density

A very important characteristic of biomass materials is their bulk density, or volume the density of the processed product impacts on fuel storage requirements.[2]

Biomass	**Bulk volume, (m^3/t, daf)**	**Bulk density, t/m^3**
Wood		
Hardwood chips	4.4	0.23
Softwood chips	5.2-5.6	0.18-0.19
Pellets	1.6-1.8	0.56-0.63
Sawdust	6.2	0.12
Planar shavings	10.3	0.10
Straw		
Loose	24.7-49.5	0.02-0.04
Chopped	12.0-49.5	0.02-0.08
Baled	4.9-9.0	0.11-0.20
Moduled	0.8-10.3	0.10-1.25
Hammer milled	9.9-49.5	0.01-0.11
Cubed	1.5-3.1	0.32-0.67
Pelleted	1.4-1.8	0.56-0.71

Table 13: Bulk volume and density of certain biomass resources.

3.7 Conversion technologies for biomass to fuels

Biomass can be converted into useful forms of energy using a number of different processes. Factors that influence the choice of process are the type & quantity of biomass feedstock.

There are three different ways of biomass conversion into useful fuels:

(i) Thermo chemical conversion
(ii) Bio-chemical/ Biological conversion
(iii) Mechanical extraction

3.7.1 Thermo chemical conversion

Within thermo-chemical conversion four process options are available:

- Combustion
- Pyrolysis
- Gasification
- Liquefaction

I. Combustion

The burning of biomass in air i.e. combustion is used over a wide range of outputs to convert the chemical energy stored in biomass into heat, mechanical power or electricity. Combustion of biomass produces hot gases around 800 – 1000°C. Combustion is feasible only for biomass with a moisture content <50%, unless the biomass is pre-dried. [44]

ii. Gasification

It is the conversion of biomass into a combustible gas mixture by the partial oxidation of biomass at high temperatures, typically in the range of 800 – 900°C. The low calorific value gas produced can be used directly as a fuel for gas turbines & gas engines. [44]

iii. Pyrolysis

Conversion of biomass to liquid, solid and gaseous fractions, by heating the biomass in the absence of air at 500°C [44]. Pyrolysis produces a liquid product called bio-oil, which is the basis of several processes for the development of the fuel, chemicals and materials. The reaction is endothermic:

Biomass +Energy → Bio-oil +Char +Gas [41]

3.7.2 Biochemical Processes

In this two main processes are used: fermentation and anaerobic digestion.

i. Fermentation

Fermentation is mostly used to produce ethanol from sugar crops. Starch is converted by enzymes to sugars and sugars to ethanol using yeasts.

ii. Anaerobic Digestion (AD)

Anaerobic Digestion is the conversion of organic material directly to a gas, termed biogas, a mixture mainly of methane and CO_2 with small quantities of other gases such as H_2S etc. Biomass is converted by bacterial in an anaerobic environment, producing a gas with energy content of about 20-40% of the lower heating value of the feedstock.[44]

3.7.3 Mechanical Extraction

This method is to produce oil from the seeds of various biomass crops, such as oil seed rape, cotton and groundnuts. This produces not only oil but also a residual solid or 'cake' used for animal fodder [44].

CHAPTER 4

LITERATURE REVIEW

4.0 Literature Review

4.1 HYDROGEN FROM BIOMASS

A summary of various processes for the production of hydrogen from biomass, as has been studied by various workers, is given in figure

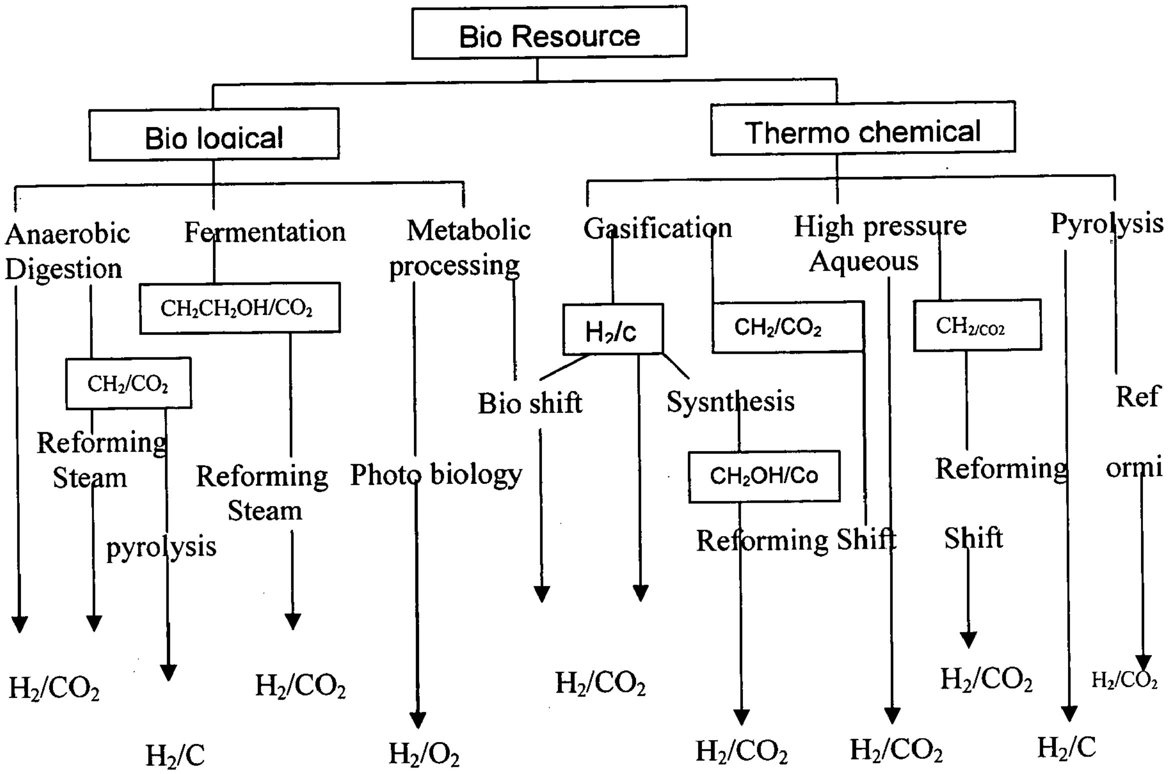


Figure 3: Pathways from Biomass to Hydrogen.
Storable intermediates are shown in boxes.

Different routes of H_2 production from biomass

Much of the hydrogen produced in the world, and especially for the petrochemical industry is obtained from natural gas, mostly made up of methane. Water electrolysis is one of the most utilized industrial processes for hydrogen production today. But also we can produce hydrogen from biomass also.

Different process routes of hydrogen-production from biomass can be broadly classified as follows:

1. Thermo chemical gasification coupled with water gas shift.
2. Fast pyrolysis followed by reforming of carbohydrate fractions of bio-oil.
3. Direct solar gasification.
4. Miscellaneous novel gasification process.
5. Biomass-derived syn-gas conversion.
6. Supercritical conversion of biomass.
7. Microbial conversion of biomass.
8. Biomass Gasification.

4.1.1 Thermo chemical gasification coupled with water gas shift

Gasification coupled with water gas shift is the most widely practiced process route for biomass to hydrogen (Figure 2). Thermal, steam and partial oxidation gasification technologies are under development around the world. Feedstock include agricultural and forest product residues of hard wood, soft wood and herbaceous species. Thermal gasification is essentially high-rate pyrolysis carried out in the temperature range of 600–1000°C in fluidized bed gasifiers. The reaction is as follows:

$$\text{Biomass} + O_2 \rightarrow CO + H_2 + CO_2 + \text{Energy}.$$

Other relevant gasifier types are bubbling fluid beds and the high-pressure high-temperature slurry-fed entrained flow gasifier. However, all these gasifiers need to include significant gas conditioning along with the removal of tars and inorganic impurities and the subsequent conversion of CO to H_2 by water gas shift reaction.

$$CO + H_2O \rightarrow CO_2 + H_2.$$

A study of almond-shell steam gasification in a fluidized bed reveals that over the range 500–800°C, smaller particle size yields more hydrogen than does higher temperatures3.

Catalytic steam gasification of biomass has also been studied in a bench-scale plant containing fluidized bed gasifier and a secondary fixed-bed catalytic reactor4. The catalytic converter using different steam-reforming nickel catalysts and dolomite can be tested over a temperature range of 660–830°C.

Fresh catalyst at the highest temperature yields 60% by volume of hydrogen. Saha *et al.*[5,6] have reported a laboratory-scale fluidized-bed auto thermal gasifier to gasify carbonaceous materials in the presence of steam. Pilot-scale experiments in the steam gasification of charred cellulosic waste material have been discussed in Rabah and Eldighidy.

It has been observed that some inorganic salts such as chlorides, carbonates and chromates have a beneficial effect on the reaction. Steam gasification was also intensely studied by many researchers at the University of Saragossa during 1984–92 (ref. 8). Fifty-seven percent (v/v) yield of hydrogen is reported using a secondary steam reformer.

Generally, conventional gasification of biomass and wastes is employed with the goal of maximizing hydrogen- production. Researchers at the Energy and Environment Research Center, Grand Forks, USA have studied biomass and coal catalytic gasification for the production of hydrogen and methane10, 11.

A brief experimental effort is described to demonstrate that the pilot-scale research on hydrogen-production by catalytic coal gasification can be extended to wood. The results show that the coal technology is fully transferable to wood, subject to minor substitution in feeding and solids-handling components. Two processes are compared using bench-scale methods to predict the approach best suited on specific coals or biomass. These are pyrolysis and subsequent cracking and steam char gasification. Catalysts can greatly enhance the efficiency of both processes.

Gasification of coal or wood catalyzed by soluble metallic cations to maximize reaction rates and hydrogen yields is said to offer a potential for large-scale economical hydrogen production with near commercial technology12. Catalysis increases gasification rates about tenfold. Catalyst screening shows that potassium-rich minerals and wood ash provide the best gas production-rate enhancement.

A number of references are available on hydrogen production by gasification of municipal solid waste13–17. Most of these focus on pretreatment of municipal solid waste to prepare slurry of suitable viscosity and heating value for efficient hydrogen-production.

Hydrothermal treatment at 300°C and mild, dry pyrolysis with subsequent slurrying are also highlighted. In the initial laboratory- scale municipal solid-waste treatment, the effects of viscosity, slurry solid content over a range of temperature and for newspapers and plastics are covered15. Development of the Texaco gasification process emphasizes on feed preparation and pretreatment18. To date, pump able slurries from an MSW surrogate mixture of treated paper and plastics have shown heating values in the range of 13–15 MJ/kg.

These process considerations can be extended to automobile shredder residues and other plastic or rubber wastes19. A study of the gasification of micro algae at 850–1000°C is described in Hirano *et al.*20. Cox *et al.*21 portray a new approach to thermo chemical gasification of biomass to hydrogen, which is based on catalytic steam gasification of biomass with concurrent separation of hydrogen in a membrane reactor that employs a perm selective membrane to separate the hydrogen as it is produced. The process is particularly well suited for wet biomass and may be conducted at temperatures as low as 300°C.

4.1.2 Fast pyrolysis followed by reforming of carbohydrate fraction of bio-oil

Pyrolysis produces a liquid product called bio-oil, which is the basis of several processes for the development of fuel chemicals and materials. The reaction is endothermic:

$$\text{Biomass} + \text{Energy} \rightarrow \text{Bio-oil} + \text{Char} + \text{Gas}.$$

Catalytic steam reforming of bio-oil at 750–850°C over a nickel-based catalyst is a two-step process that includes the shift reaction:

$$\text{Bio-oil} + H_2O \rightarrow CO + H_2.$$

$$CO + H_2O \rightarrow CO_2 + H_2.$$

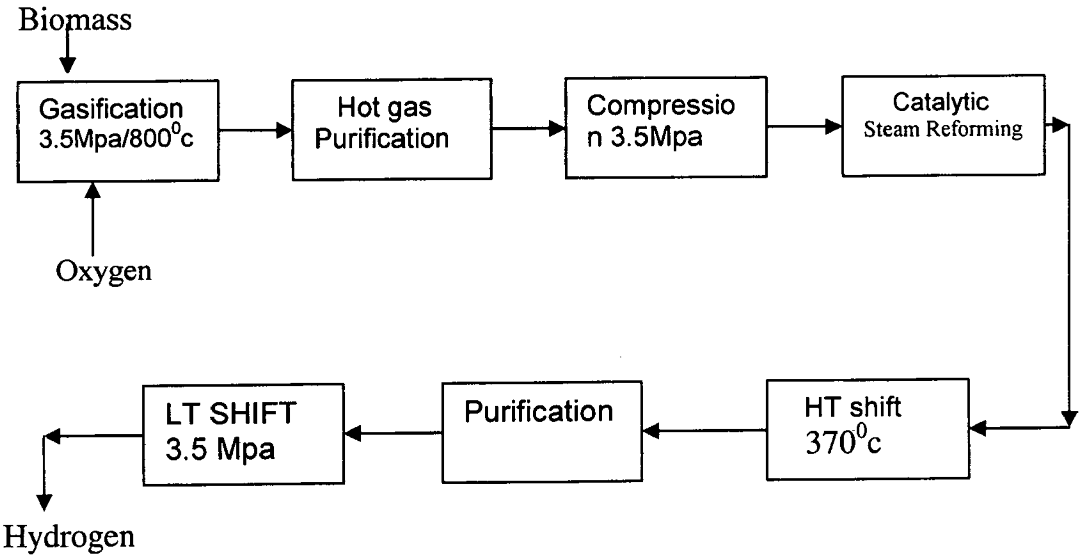


Figure 4: Overall flow diagram for hydrogen production from biomass. HT, High temperature; LT, Low temperature; PSA, Pressure swing adsorption.

The overall stoichiometry gives a maximum yield of 0.172 g H2/g bio-oil (11.2% based on wood).

$$CH_{1.9}O_{0.7} + 1.26\ H_2O \rightarrow CO_2 + 2.21\ H_2.$$

The first step in pyrolysis is to use heat to dissociate complex molecules into simple units. Next, reactive vapors, which are generated during the first step, convert to hydrogen. The Waterloo fast-pyrolysis process technology carried out at 700°C is used for the steam gasification of pine sawdust using Ni–Al catalyst at a molar ratio 1 : 2. It has revealed that catalytic reactivation and high steam to biomass ratios diminish the rate of deactivation22. Methanol and ethanol can also be produced from biomass by a variety Of technologies and used on board reforming for transportation.

Caglar and Demirbas23 have used pyrolysis of tea waste to produce hydrogen, while Abedi *et al.*24 have studied hydrogen and carbon production from peanut shells.

4.1.3 Direct solar gasification

In 1974, Antal *et al.*25 examined the feasibility of using solar process heat for the gasification of organic solid wastes and the production of hydrogen. A detailed review with many references of the technology describes solar gasification of carbonaceous materials to produce a syngas quality intermediate for production of hydrogen and other fuels26.

Shahbazov and Usupov27 have shown good yield of hydrogen from agricultural wastes using a parabolic mirror reflector. The use of a palladium diaphragm in this respect is reported to achieve solar-assisted hydrogen separations from the gases generated by pyrolysis of hazelnut shells at 500–700°C (ref. 28).

Walcher *et al.*29 have mentioned a plan to utilize agricultural wastes in a heliothermic gasifier.

4.1.4 Miscellaneous novel gasification processes

Several novel heat sources and chemistries have also been explored for hydrogen from organic biomass. Safrany30 has proposed the use of a thermonuclear device to vaporize waste organic materials in an underground, large-scale plasma process.

In the 1980s, two novel processes for hydrogen from carbonaceous materials were presented. Thakur31 tested the production of hydrogen by the electrolysis of a mixture of coal, lime and water.

In 1981, an open-cycle two-step process was tested involving the reduction of In2O3 by carbon (chars) and its re oxidation by water to produce hydrogen32.

$$In_2O_3 + C \text{ (or } 2C) \rightarrow In_2O + CO_2 \text{ (or } 2CO) \qquad T > 873 \text{ K.}$$

$$In_2O + 2H_2O \rightarrow In_2O_3 + 2H_2 \qquad T < 673 \text{ K.}$$

A set of biochemical reactions have been proposed to describe decomposition of water into hydrogen and oxygen using nuclear heat and a carbon cycle 33.

Municipal waste is suggested as a possible source of carbon. Algae can be a by-product. Coughlin and Farooque34 have showed that coals and other forms of solid carbonaceous fossil fuels could be oxidized to oxides of carbon at the anode of an electrochemical cell and hydrogen produced at the cathode. Gases produced are discussed as function of coal slurry concentration and electrode potential.

4.1.5 Biomass derived syn-gas conversion

Hydrogen production from gasified biomass by sponge iron reactor is also reported 35, 36. The sponge-iron process (or steam-iron process) offers a simple possibility to store the energy of synthesis gas. A number of recent studies have looked into the classical steam-iron process for upgrading synthesis gas (mainly CO and H2) to pure H2 for use in fuel cells and other energy devices. Friedrich *et al.*37 worked on the purification of nitrogen containing reduction gas from a biomass gasifier using wood and wood waste. The process involves two steps: (1) Cleaning of gas from solid biomass or coal or methane, and (2) energy storage in sponge-iron. This study investigates woody biomass and commercially available sponge-iron.

The reactions are:

$$Fe_3O_4 + 4CO \rightarrow 3\,Fe + 4\,CO_2 \text{ (coal, biomass or natural gas)}$$

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2.$$

Kniplles *et al.*38 present laboratory and pilot-plant data showing the technical feasibility of hydrogen recovery from biomass gasification lean mixtures (e.g. producer gas).

4.1.6 Supercritical conversion of biomass

Many researchers have investigated the aqueous conversion of whole biomass to hydrogen under low temperature but supercritical conditions. The earliest report of supercritical gasification of wood is by Modell39.

He studied the effect of temperature and concentration on the gasification of glucose and maple sawdust in water, in the vicinity of its critical state (374°C, 22 MPa). No solid residue or char is produced. Hydrogen gas concentration up to 18% (v/v) is reported.

The first report of extensive work on supercritical conversion of biomass-related organics was given by Manarungson *et al.*40, where glucose at 550°C and 5000 pound per inch2 guage (Psig) has been converted largely into hydrogen and carbon dioxide. This was followed by a study of the uncatalyzed solvolysis of whole biomass and hemi cellulose in hot compressed liquid water41.

The first study showed that complete gasification of glucose can occur at 600°C, 34.5 MPa and 30 s residence times. Inconel strongly catalyses the water gas shift reaction42. Following this work, a flow reactor has been used with newly discovered carbon-base catalysts to convert water hyacinth, algae, pithed bagasse, liquid extract, glycerol, cellobiose, whole biomass feedstock and sewage sludge to hydrogen. Wood sawdust, dry sewage sludge or other particulate biomass can be mixed with a corn-starch gel to form a viscous paste. This paste can be delivered to a supercritical flow reactor with a pump. Ongoing work indicates that the starch can be reduced to 3% (w/w) and the particulate biomass increased to 10% (w/w). At the critical pressure of water (22 MPa), the paste vaporizes without the formation of char. A packed bed of carbon catalyst, at 650°C, causes the tarry vapors to react with water to produce hydrogen, carbon dioxide, some methane and only a trace of carbon monoxide43.

Experimental

All the work of supercritical water extraction was performed in a 100ml cylindrical autoclave made of SS-316. The sample was loaded from the bolt hole into the autoclave. Figure 4.2 shows the SWE system [15].

Reaction System

A pilot Plant at the University of Twente (Netherlands) with a capacity up to 100Kg feedstock per hour is taken as the reference for the scheme of the supercritical water gasification (SCWG) process.

Super critical water gasification process consists of main units as feed pumping, heat exchanger (HE), reactor, high pressure gas liquid separator (SI), low pressure gas liquid separators (S2 and S3). For high purity hydrogen production, Pressure Saving Adsorption (PSA) or hydrogen membranes may be the options.

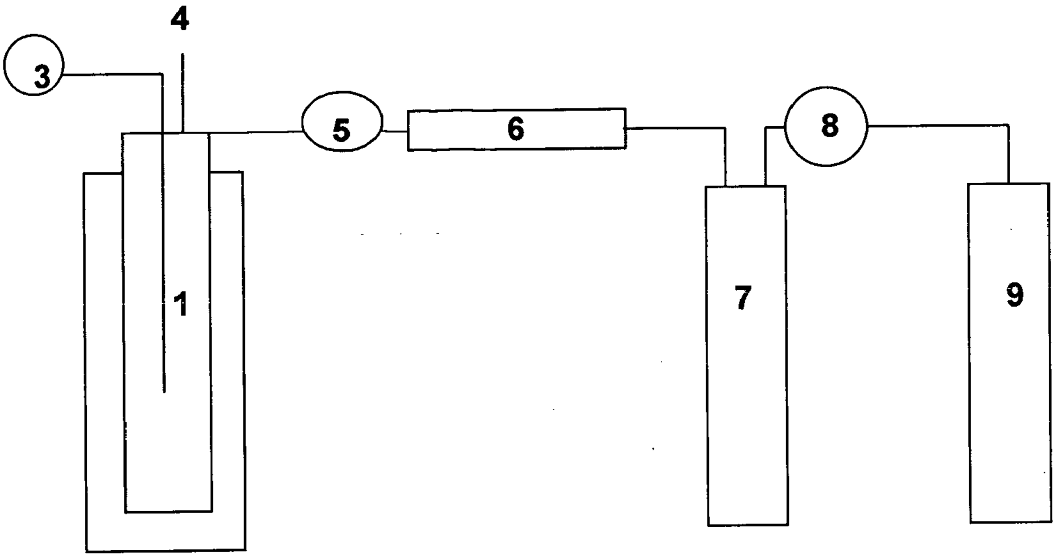


Figure 5: Supercritical water extraction system. (1) Autoclave, (2) Electrical Furnace, (3) Temperature control monitor, (4) Pressure control monitor, (5) Product exit value, (6) Condenser, (7) Liquid collecting vessel, (8) Gas cleaning, (9) Product gas collecting vessel.

The autoclave is supplied with heat from external, heater and power is adjusted to give an appropriate heating time. Figure 4, [16]

Phase equ. For biomass conversion processes in sub critical and super critical water, Chemical Engg. Journal 98(2004) 105-113, pp. 110, Fig. 9)

4.1.7 Microbial conversion of biomass

Highly concentrated organic wastewater is one of the most abundantly available biomass, which can be exploited for microbial conversion into hydrogen. A new and unique process has been developed when a consortium of bacteria ferments substrates such as carbohydrates; they produce hydrogen and carbon dioxide.

Municipal solid wastes and digested sewage sludge have the potential to produce large amount of hydrogen by suppressing the production of methane by introducing low voltage electricity into the sewage sludge.

Fascetti and Todini44 have reported on the photosynthetic hydrogen evolution from municipal solid wastes. Batch-wise and continuous experiments show that the acidic aqueous stream obtained from such refuse is a good substrate for the growth of *R. sphaeroides* RV. The substrate from the acid genesis of fruit and vegetable market wastes gives higher hydrogen evolution rates (about threefold) compared to synthetic medium.

Mixed culture of photosynthetic anaerobic bacteria provides a method of utilization of a variety of resources for hydrogen-production45. Hydrogen production from whey by phototropic bacteria like *R. rubrum* and *R. capsulatus* has been discussed by Venkataraman and Vatsala46. Roychowdhury *et al.*47 have on reported hydrogen generation from fermentative bacteria.

Kumar and Das48 studied the suitability of starchbased residues for hydrogen-production. Lactate and lactate-containing waste water49, cow dung slurry50, vegetable starch, sugar-cane juice and whey51, bean-product waste water52, tofu waste water53 are among other liquid biomass which are extensively used for hydrogen production.

Nitrogenease

It is a two component portion system that was MgATP (2ATP/e^-) and low potential electrons derived from reduced ferrodoxin or flavodixin to reduce a variety of substrates. In the absence of other substrates it continues to turnover, reducing proton to hydrogen.

This is the basis of hydrogen production by nitrogenease. AT each cycle, MgATP complexed Fe – proteins associates with MoFe-protien, 2ATP are hydrolyzed with the transfer of one electron to MoFe –protein and the complex dissociates.

Hirano et.al (1998) (Japan) studied the gasification of micro-algae 850-1000C.

Ni Fe Se Hydrogenease:

Many microorganisms have been shown to contain a NiFe or NiFeSe hydrogenase, which is usually thought of functioning as an "uptake" hydrogenase that is a hydrogenase whose normal metabolic function is to derive reductant from H_2. Electrons derived from H_2 are used, either directly, or indirectly through the unique pool , to reduce NAD(P). The NiFe hydrogenases are heterodimeric proteins consisting of both small (S) and large (L) sub-units.

The small sub-units contains three Fe-S cluste, two [4Fe-4S] and one [3Fe-4S] . The large subunits contain a unique, complex NiFe center with coordination to 2CN and 1CO, forming a biologically unique metallocenter.

Fermentative Hydrogen Production

Hydrogen can be produced by dark, anaerobic bacterial growth on carbohydrates rich substrates giving organic fermentation end products, H_2 and CO_2. Pure cultures found to produce hydrogen from carbohydrates includes species of Enterobactor, Bacillus and Chlostridium. The pure substrates used include glucose, starch and cellulose. Process conditions including inoculum have a significant effect on H_2 yield, as they influence the fermentation end products. Carbohydrates are the preferred organic carbon source for H_2 production. Glucose in biomass gives a yield of $4H_2$ per glucose when acetic acid is the by-product. [18]

$$C_6H_{12}O_6 + 2H_2O_2 \rightarrow 2\ CH_3COOH + 2CO_2 + 4H_2$$

$$C_6H_{12}O_6 \rightarrow CH_3\ CH_2\ CH_2\ COOH + 2CO_2 + 2H_2$$

4.1.8 Biomass Gasification

Gasification is the conversion of biomass into a combustible gas mixture by the partial oxidation of biomass at high temperatures, typically in the range of 800–900C. Gasification is the process of partial oxidation to convert carbonaceous feedstock into gaseous energy carrier consisting of permanent, non-condensable gas.

In an ideal gasification process biomass is converted completely to CO and H_2 although in practice some CO_2, water and other hydrocarbons including methane are formed. Most simple biomass gasifiers produce approximately equal proportions of CO and H_2.

This is a conversion process, which converts a solid biomass fuel into a gaseous energy carrier (CO, CO_2, CH_4, H_2 and H_2O). The main reaction steps in biomass gasification are:

- Heating and Pyrolysis of the biomass whereby converting biomass into gas, char & primary tar.
- Cracking of primary tar to gasses and secondary and ternary tars.
- Cracking of secondary & tertiary tars.
- Heterogeneous gasification reactions of the char formed during pyrolysis and homogeneous gas phase reactions.
- Combustion of char formed during pyrolysis and oxidation of combustible

In a gasification processes, the solid fuels are completely converted (except the ashes in the feed) to gaseous products having different compositions. Because of the production of cleaner gaseous fuel as well as almost complete conversion of biomass, the gasification process is converting biomass into energy is becoming attractive day by day.

The char produced from the fast pyrolysis of biomass is highly reactive and can be gasified with gasifying agents such as steam, CO_2, oxygen & H_2 to gaseous fuels. Recently there is lot of interest in utilizing the pyrolysis derived char for steam gasification to produce gaseous fuel. The composition of gas produced during steam gasification of char depends on the inherent nature of the char and the process conditions employed during the gasification process.

Air gasification: Air gasification is most widely used technology since a single product is formed at high efficiency and with out requiring oxygen. A low heating value gas is produced of up to 60% N_2 with a typical heating value of 4-6MJ /Nm^3 with byproducts such as water, CO_2, hydrocarbons, tar, and N_2. The temperature of 900-1100 C is achieved.

i. O_2 Gasification:

Yields a better quality gas of 10-15MJ/ Nm^3. In this process relatively a temperature of 1000-1400C is achieved. But it requires an O_2 supply with concomitant problem of cost and safety.

ii. Steam gasification:

Biomass steam gasification results in the conversion of carbonaceous material to permanent gases (H_2CO, CO_2, CH_4 and light hydrocarbons), char and tar. To avoid corrosion problems, poisoning of catalysts and to improve the overall efficiency of the gasification process, tar components needs to be minimum.

Turn et.al 1998 (USA) reported results from their bench scale fluidized bed non-catalytic gasifier. For sawdust the highest yield was obtained at 800C and equivalence ratio of 0.0 and a steam to biomass ratio of 1.7.

Cypres (1987) (Belgium) discussed metallurgical processes for the hydrogen production from coal and other carbonaceous materials.

4.1.8.1 Reactor Systems for Gasification

For thermo-chemical processes, different reactor designs are needed. One possibility is to characterize reactor types is based on the type of transport of fluids or solids through the reactor [19]. The four main types are –

- Quasi – non moving or self moving feed stock
- Mechanical moved feedstock
- Fluidic ally moved feedstock
- Special reactors

Two of mainly used reactor types for the gasification of biomass are fixed bed reactor and fluidized bed. Fixed bed rectors Figure 5.1 can have countercurrent, co current or very seldom-cross current mass flow. Counter current mass flow means that the feedstock and the reactive material flow in opposite directions.

For fluidized bed gasification of biomass of two types are bubbling and circulation bed [19] Figure 6.

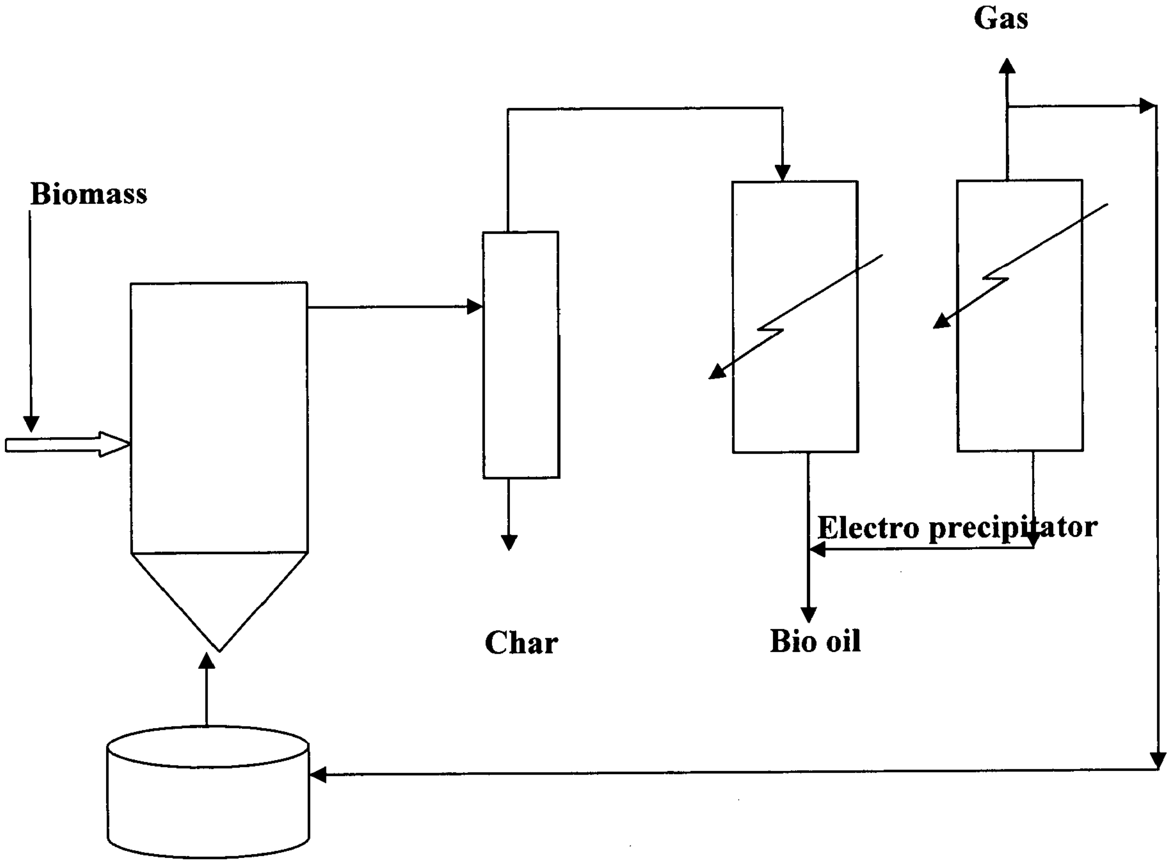


Fig 6: Fluidized bed gasification of biomass

i. Multistage circulating fluidized bed reactor

In this a multistage reactor is presented designed especially to overcome number of problems usually encountered in circulating fluidized bed gasification of biomass. The novel reactor is a riser built up of several segments, each being constructed from two opposite cones welded together [20].

Tubes with a diameter equal to be base diameter (D_0) of the cones interconnect the segments. It is important to note that this new reactor is a co-current multistage fluidized bed. The precise nature of fluid beds depends of course on the applied gas flow rate through the reactor, the properties of solids and the geometry of the reactor segments.

ii. *LU Pressurized Fluidized Bed Air Blown Gasifier*

The gasification test consists of four main units: a bubbling pressurized fluidized bed gasifier, a hot gas filtration unit, a catalytic conversion unit and a pressurized feeding unit. The test rig is designed for operations temperatures the hot gas filter unit and the catalytic conversion unit are placed inside three cylindrical pressure vessels of 0.5m inner diameters. The fluidized bed reactor consists of a tube 102mm inner diameter having a total length of about 3.3m. Air as fluidizing agent is feed into the reactor bottom through a funnel shaped inlet.

The feedstock is introduced by a screw feeder about 300mm from the bottom end. The reactor tube is surrounded by six electrically heated furnaces. The furnaces supply the desired heat to the reactor to achieve the ignition temperature during the start up phase. During the gasification these heaters can to some extent, adjust the reactor temperature.

The gasifier is equipped with a continuous fuel feeding system. Biomass fuels is fed into a compression unit and compressed by hydraulic piston to its half the original volume. The pressure in the reservoir is same as that of the gasifier [5].

iii. Two Stage Gasification Reactor for Bagasse

Bagasse is considered a difficult fuel due to its fibrous nature, low bulk density and high moisture content. The high efficiency fluidized bed technology cannot be directly applied to bagasse due to the difficulties associated with its fluidization. A two-stage gasification reactor is proposed for bagasse gasification. The apparatus consists of two quartz stages, indirectly heated, and separated by the feeder. Stage one is a free fall reactor with a quartz frit on the bottom side working as an updraft gasifier.

Stage two is a fixed bed-reforming reactor. The feed was introduced in the reactor through a piston [21].

Mechanism

As soon as biomass enters the reactor system it falls by gravity into stage 1. Due to high temperature it immediately dries and pyrolyzes. The volatile components are released and char formed goes to the bottom of stage 1 and reacts with the oxidizing mixture consisting of steam & oxygen. Solid ashes and mixture of gases are formed composing CO_2, CO, H_2, water vapor, pyrolysis product, tar & hydrocarbons. The mixture goes to stage 2 where tar & heavy Hydrocarbons, trapped in bed, increase their residue time allowing for complete gasification.

iv. Biomass gasification in Atmospheric Bubbling Fluidized Bed

Thermo chemical gasification is a well-known technology, which can be classified depending on the reactor type (bubbling or circulating fluidized beds), its pressure or gasifying agent. Between these technologies /or processes the atmospheric biomass gasification with air in a fluidized bed seems to have a feasible application in some scenarios. It is studied in a small pilot plant. Equalence ratio was 0.20 to0.45, and the temperature of gasifier was 750-880^{0}C.

This installation is based on a fluidized bed gasifier with a throughput of 200-300Kg/h.m^2

The reactor is a bubbling fluidized bed of 6cm I'd. The biomass is fed at the bottom of the bed near the distributor plate. Operating temperatures are 700-800C. Details of the feeding systems used are given below in Table 12.

Particle size, mm	-4.0 - 0.80
Proximate analysis(wt%)	
Volatile matter	81-83
Fixed carbon	16-17
Ash	0.5-1.2
Ultimate elemental analysis(wt%)	
Carbon	50.0
Hydrogen	5.7
Oxygen	44.1
Nitrogen	0.1-0.3
Sulfur	0.03
LHV(MJ/Kg of daf fuel)	18.0-18.4

Table 13: Feedstock (pine saw-dust) analysis (dry basis)

v. Gasification of Carbonaceous Waste

Gasification of carbonaceous liquid wastes such as waste oil or waste organic solvents and solid carbonaceous waste such as coal and shredded waste tire means converting C and H contained in the organic materials into fuel gases, CO and hydrogen gas.

Since gasification is an endothermic reaction requiring a continuous supply of heat, the gasification furnace should be kept at high temperature to sustain the reaction. in conventional gasification methods, oxygen is supplied with carbonaceous compounds to the gasification reactor, thereby inducing the oxidation of C and H components in the carbonaceous feed stocks .

The oxidation reaction is: The gasification reactions of organic materials are the following: 23

$C+O_2 \rightarrow CO_2$ (1)

$2(-CH_2)+3O_2 \rightarrow 2H_2O+2CO_2$ (2

$C + H_2O \rightarrow CO + H_2$ (3)

$C + CO_2 \rightarrow 2CO$ (4)

$(-CH_2) + H_2O \rightarrow CO + 2H_2$ (5)

$(-CH_2) + CO_2 \rightarrow 2CO + H_2$ (6)

Symmetrically the constitution and the mechanism of the gasification reactor according to the present work. As shown herein, gasification reactor 1 is composed of two parts of the same shape and size which re connected to each other vertically. The lower end of the reactor 1 is an oxidation reaction chamber while the middle portion of the reactor 1 is reduction reaction chamber. The reduction chamber is where the reactions 3-6 occur. Reactor1 has a center of diameter of 6cm and a height of 150cm. The reactors inner cavity is aligned with 5 cm thick molded Cerak wool and shielded with 5cm thick blanket of the same and then 3mm SS casing.

In the reduction reaction chamber of the reactor 1, a liquid feed nozzle 2 for spouting liquid waste such as waste oil into the reactor 1,a solid waste supply nozzle 3 for supplying solid waste coal powder into reactor 1 using a screw feeder, and a steam supplier 4 for spouting steam into the reactor 1 are equipped.

A liquid feed heater is connected with the liquid feed nozzle 2 for heating the liquid feed supplied into the reactor 1, and a water heater 6 is connected with the steam supplier 4 for supplying water into the reactor 1 as steam. An outlet 7 for discharging produced syngas from the reactor 1 is provided in the upper end of the reactor 1. Close to the produced syngas recycling tube 8, an oxygen supplier 9 is equipped at the lower end of the reactor 1 in the oxidation reaction chamber for supplying O_2 required to react with the produced syngas.

Reactor 101:

Gasification reactor 101 is simplified structure of reactor 1 and has a syngas burner equipped in the body of gasification reactor. In the body of gasification reactor 101, a screw press feeder 102 is equipped at the bottom of the reactor 101 for the supplying solid feed into the reactor. An outlet 103 for discharging produced syngas from reactor 101 is provided in the upper end of the reactor 101, and an ash trap 104 is provided in the power end of the reactor 101 for storing molten salt flowed out from the reactor. Ash trap 104 is inter-changeable with solid feeder 102. Further, the body of the reactor 101 is equipped with a syngas burner 105 which replaced the oxidation reaction chamber of reactor 1.

One syngas burner on each side, i.e., two syngas burner is equipped in reactor 101. On the wall of the reactor 101, thermocouples points 106 are installed for measuring the temperature in reactor 101, and heat exchanger 107 is installed for cooling the produced syngas discharged from the upper portion of the reactor 101 to recover the heat. Further, a produced syngas recycling tube is also provided in the body of the reactor 101.

Schematically the constitution of the syngas burner that is connected with the gasification reactor shown in. for supplying syngas or H_2 gas and a tube 109 for supplying O_2 are fixed by flange 110, and the tubes are surrounded by an insulating material 111 and 111B (cerak wool mold and blanket) Pipe 112 is placed so that a stick of pilot light is inserted for ignition [23].

Saha et.al. (1982,1984) (India) reported using a laboratory scale fluidized bed auto thermal gasifier to gasify carbonaceous material in steam. Further studies with agricultural wastes were planned. Cocco and Costantinides (1998) (Italy) describe the pyrolysis gasification of biomass to hydrogen. From 1994-1997 researchers from Lawrence Livermore National Laboratory pursued hydrogen production by the gasification of municipal solid waste.

vii. Countercurrent Fixed Bed Gasifier

A laboratory scale countercurrent fixed bed gasification plant has been designed and constructed to produce data for process modeling and to compare the gasification characteristics of several biomasses (beech wood, nutshells, olive husks, and grape residues). [24]

Two main classes of chemical reactors, fixed bed and fluid bed reactors are applied for biomass gasification. Fixed bed countercurrent (updraft), and countercurrent (downdraft) reactors are, in general of very simple construction and operation. They also present high carbon conversion, long solid residence times, and low ash carry over. On the other hand updraft process is more thermally efficient than the downdraft process but the tar content of gas is very high. Updraft gasification technology is investigated, though several updraft fixed bed plants are in operation in Northern Europe for peat & wood chip gasification.

A laboratory scale gasification plant has been shown in Figure 5.9.

The composition of the dry gas for beech wood and agricultural Residues is shown in Table 13.

Biomass	Wa [kg/h]	CO [vol%]	CO_2 [vol%]	H_2 [vol%]	CH_4 [vol%]	HHV
Beechwood	1.560-2.340	28.6-30	7-5.5	7-7	1.8-1.8	5.35-5.5
Nutshells	1.560-1.950	28.4-30	7-6.7	7.3-6	1.7-1.9	5.3-5.6
Olivehusks	1.560-1.716	26-28.5	7.5-6.2	6.4-8	1.4-1.6	4.8-5.5
Grape residues	1.560-1.716	26-28	8-6	7-7.7	0.7-0.75	4.6-4.9

Table 14: Composition of the dry gas for Beachwood and Agricultural Residues

Counter current gasification of wood and agricultural residues (nutshells, olive husks, grape residues, 2 straw pellets) at laboratory scale has been carried out.

viii. Open Top Re-burn down Draft Gasifier

The biomass gasification technology package consists of a fuel and ash handling system, gasification system reactor, gas cooling and cleaning system. Typical gasifier system configuration is shown in Figure (5.9) [25]. (Biomass gasification tech a route to meet energy needs special section pg909 fig1))

The novel open top down draft reactor design is a ceramic lined cylindrical vessel with a bottom screw for ash extraction. The dual air entry from top and the nozzles permits establishing front moving propagation towards the top of the reactor.

Midilli et.al. (2001) (U.K) are studying the use of an air blown, downdraft gasifier for Hazelnut shells.

ix. Gasification in Down Draft Fixed Bed

Comprehensive test runs were carried out in a fixed bed down draft gasifier Figure (5.10) [26]. Using some common European biofuels (oak, turkey oak, almond shells), Experiments were done in a 129 KW_{1-h} gasifier operating in downdraft mode utilizing air as the gasifying agent. The plant is a double wall cylindrical chamber whole combustion zone is made up of stainless steel.

(Energy & fuels, Vol. 14, No.4, 2000, 889 – 898, pp. 891, fig.1)

x. Steam gasification of char

Char from fast Pyrolysis System

Some reasonable amount of char is produced during the fast pyrolysis of biomass. This char is highly reactive and can be gasified with gasifying agents such as steam, CO_2, oxygen & H_2 to gaseous fuels. Recently there is lot of interest in utilizing the pyrolysis-derived char for steam gasification to produce gaseous fuel.

The composition of the gas produced during steam gasification of the char depends on the inherent nature of the char and the process conditions employed during steam gasification.

The steam gasification experiments were carried out in a down flow reactor Figure 6.1 [4]. (Energy & Fuels, vol. 15, No. 3, 2001, P-737)

It consists of a pre-heater to vaporize water into steam, an inconell reactor (450mm long and 11mm i.d.) with temperature controller, a metering pump, a liquid collection trap, and a gas collection system.

Bakshi and associates (1999) (Canada) presents results from steam gasification of lignin, biomass chars and Westvaco Kraft Lignin to hydrogen and high and medium bitumen gas. Three lignins Kraft-1, Kraft-2 and Alcell were gasified at 600-800 in a fixed bed with steam flow rate of 10g/h/g of lignin. Hydrogen contents ranged from 30-50%.

Sato and White conducted experiments on gasification of Texas lignite and platinized titania in the presence of water vapor and UV light for the production of H_2 andCO_2.

Char & Lignin from Different Sources

Char A, Supplied by ENSYN Technologies Inc. of Ohawa Canada, Char B from catalytic upgrading of bio oil using HZSM-5 catalysts, were gasified [37].

Lignin (kraft 1) obtained from spruce wood at Irving Pulp and Paper Company and Lignin used for converting to hydrocarbons, i.e. Alcell Lignin was also gasified.

Steam gasification of chars was carried out at atmospheric pressure in a continuous down flow fixed bed micro reactor operated at 600, 700 & 800°C. The reactor was 500 mm long, 11 mm i.d.

4.1.9 Catalytic Pyrolysis/ gasification

Pyrolysis is an important process for obtaining energy from biomass. Valuable gases such as H_2 and CO, can also be generated by pyrolysis. There are three stages of this process. First consists in the catalytic steam reforming of pyrolysis liquids to produce H_2.

Second, the pyrolysis process is carried out around 700°C and this stage also includes the removing of the tar content of the gas and improving the quality of the product gas.

In the second stage catalysts, normally dolomites & Ni catalysts high temperatures, steam and oxygen could be used.

In the third option the pyrolysis occurs at a lower temperature (<750°C) and catalyst is incorporated in the same reactor where the pyrolysis of biomass occurs. Pacific North West laboratory studied the gasification of biomass to produce a variety of gaseous fuels by use of appropriate catalysts.

Catalysts

Various types of catalysts, such as nickel based catalysts, dolomites, zeolites, etc. can be used. Most studies used a catalyst in the secondary reactor where the volatile tar, is cracked down to the product gas on the catalyst surface in the presence of gasifying agent [6].

Dolomite and steam reforming Ni based catalysts are the most conventional and active catalysts for tar cracking at 1073 – 1173K for dolomite and 973 – 1073K for Ni based catalyst.

Various types of oxide catalysts were also studied, CeO_2 was found to be a better one. It was incorporated as $Rh/CeO_2/SiO_2$. In case of cedar wood biomass, it gave 98% conversion into gaseous product. The gasification of cellulose has been investigated on Rh catalyst supported on CeO_2, ZrO_2, Al_2O_3, TiO_2, MgO and SiO_2 at very low temperatures (723-823K).

Effect of various supports and supported metal catalysts is given in Table 14. [12]

	Yield of gases, Wt%						
Catalyst	CO	H_2	CO_2	CH_4	C_2H_6	H_2/CO	C to gas (wt%)
None	160	90	790	30	5	0.6	53
CeO_2	330	630	860	120	5	1.9	71
MgO	260	430	960	60	24	1.7	70
TiO_2	240	560	1040	40	7	2.3	71
ZrO_2	180	490	1020	110	7	2.7	71
Al_2o_3	200	480	720	60	8	2.4	53
SiO_2	220	230	680	60	9	1.0	52
Rh/CeO_2	670	1290	1060	120	3	1.9	100
Ru/CeO_2	490	1010	1050	130	4	2.1	91
Pd/CeO_2	360	830	1180	70	5	2.3	87
Pt/ CeO_2	360	850	1080	120	4	2.3	85
Ni/ CeO_2	280	740	1150	50	4	2.6	80
G-91	450	760	990	180	4	1.7	87
Rh/CeO_2	370	920	1160	300	15	2.5	100
Rh/ZrO_2	450	680	1150	250	9	1.5	98
Rh/Al_2O_3	340	660	1210	260	7	1.9	98
RhTiO_2	220	800	960	370	2	3.6	84
Rh/MgO	360	820	1010	170	4	2.3	83
Rh/SiO_2	400	720	698	160	3	1.8.	68

Table15: Effect of various supports and Supported metal catalysts on gasification of cellulose.

Catalyst can be placed into the pyrolysis reactor in two ways, one in the layer of glass wool and the other in the mix with the original biomass particles prior to the experiments.

- Another catalyst $NiAl_2O_4$ was used for the catalytic gasification of biomass with Ni content of 33%. It is a green crystalline compound with bulk density 1100 kg/m^3.

- Cu based catalysts can also be used to produce H_2 by steam reforming of methanol at temperatures over 550 K. [14]

The catalysts are also compared based on their selectivity for H_2 production. Silica supported Rh, Ru and Ni show low selectivity for production of H_2 while Pt, Ni and Ru exhibit high activities for the reforming reaction, only Pt & Pd show relatively high selectivity for the production of H_2.

Another catalyst, Rhodium hydro-calcite ($Mg_4Rh_{0.48}Al_{1.95}O_7$) has been successfully used for the production of syngas by partial oxidation of methane.

Reactors used

The bench scale gasification unit is used for biomass conversion using catalyst Ni Al_2O_4 **(Fig. Energy & Fuels, Vol. 8, No.6, 1994, pg. 1194.)** having the Ni content of 33% [13]. N_2 or CO_2 was used to transport the wood particles continuously into the reactor at feed rates of 10-100 g/h. The process was operated at room temperature. Gasification test are carried out at comparable conditions at 500, 600, 650 and 700°C using Ni-Al-catalyst. Results are provided in Table 14. [13]

	Run No.				
	G-42	**59**	**115**	**148**	**155**
Feed rate ,g/min	---	0.46	0.49	0.45	0.46
Temperature ,C	497	500	600	650	700
Wt of catalyst in run ,g	Sand	48	43.4	44.6	43.1
F/C ,h-1	0.53	0.58	0.65	0.58	0.61
Residence time , s	0.63	0.80	0.78	0.81	0.80
Yields, wt % mf feed					
Gas	14.0	72.93	84.78	82.27	90.12
Water	12.2	-2.95	-1.62	-2.97	-3.68
Tar	61.1	5.39	0.37	0.00	0.00
Solids(char, coke,soot)	14.7	21.40	14.94	15.67	14.11
Recovery	102.0	96.07	98.44	99.93	100.36
Gas yields ,wt % feed					
H_2	-----	3.56	4.20	5.28	4.27
CO	5.03	24.47	53.73	63.52	68.25
CO_2	6.96	37.77	19.70	12.13	10.20
CH_4	0.34	6.46	2.98	2.08	2.16
C to gas , wt %	-----	50.4	64.9	67.4	71.9
H_2/CO vol ratio	-----	2.00	1.08	1.15	0.86
Vol% (H_2 +C),N_2 free	-----	68.5	86.02	92.4	92.6

Table 16: Experiments at different temperatures

Also Table 15 shows the effect of gasification media, i.e. using Ni-Aluminates catalyst, with N_2, N_2 steam, CO_2 and CO_2 steam

	Run No.				
	123	**117**	**127**	**129**	**147**
Feed rate ,g/min	0.48	0.51	0.58	0.57	0.45
Temperature ,C	650	650	650	650	650
Wt of catalyst in run ,g	42.0	43.4	42.4	43.8	44.8
F/C ,h-1	0.65	0.68	0.78	0.75	0.74
Atmosphere	N_2	N_2 steam	N_2 steam	CO_2	CO_2 steam
Ratio steam/wood ,g	NA	1:6.7	1:4.4	NA	1:7.2
Residence time ,s	0.83	0.77	0.70	0.74	0.74
Yields, wt % mf feed					
Gas	83.74	96.92	109.97	A	A
Water	-3.36	-14.18	-22.18	A	A
Tar	0.00	Tr.	0.00	0.00	0.00
Solids(char, coke,soot)	16.98	11.79	12.20	6.08	8.18
Recovery	97.36	94.5	99.99	----	----
Gas composition% of feed as is					
H_2	4.36	3.58	6.14	0.24	0.19
CO	58.46	56.87	68.53	16.07	12.24
CO_2	14.46	27.20	27.17	84.39	92.61
CH_4	2.37	4.66	2.70	0.00	0.00
%C to gas	65.1	73.9	82.2	88.7	83.5

Table 17: Experiments with different gasification media

It was found that use of CO_2 steam leads to complete gasification of even the secondary char produced.

4.2 Comparative analysis

A comparison of different process routes for hydrogen production on the basis of their relative merits and demerits is given in Table 4. In all types of gasification, biomass is thermo chemically converted to a low or medium-energy content gas. Air-blown biomass gasification results in approximately 5 MJ/m3 and oxygen-blown 15 MJ/m3 of gas. However, all these processes require high reaction temperature. Char (fixed carbon) and ash are the pyrolysis by-products that are not vaporized. Some of the unburned char may be combusted to release the heat needed for the endothermic pyrolysis reactions. For solar gasification, different collector plates (reflectors) like parabolic mirror reflector or heliostat are required. In supercritical conversion, no solid residue or char is produced in most of the cases. A wide variety of biomass is nowadays being used to produce hydrogen using supercritical water. In microbial conversion of biomass, different waste materials can be employed as substrates. These wastes are also treated simultaneously with production of hydrogen.

Process	Merits	Demerits
Thermo chemical gasification	Maximum conversion can be achieved	Significant gas conditioning is required Removal of tars is important
Fast pyrolysis	Produces bio-oil which is the basis of several processes for development of fuels, chemicals and materials	Chances of catalyst deactivation
Solar gasification	Good hydrogen yield	Requires effective collector plates
Supercritical conversion	Can process sewage sludge, which is difficult to gasify	Selection of supercritical medium
Microbial conversion	Waste water can also be treated simultaneously. Also generates some useful secondary metabolites	Selection of suitable microorganisms

Table 18: Merits and demerits of different processes of biomass conversion to hydrogen

CHAPTER 5

EXPERIMENTAL SET UP

5.0 Experimental Set up

5.1 DIAGRAM OF THE WHOLE UNIT

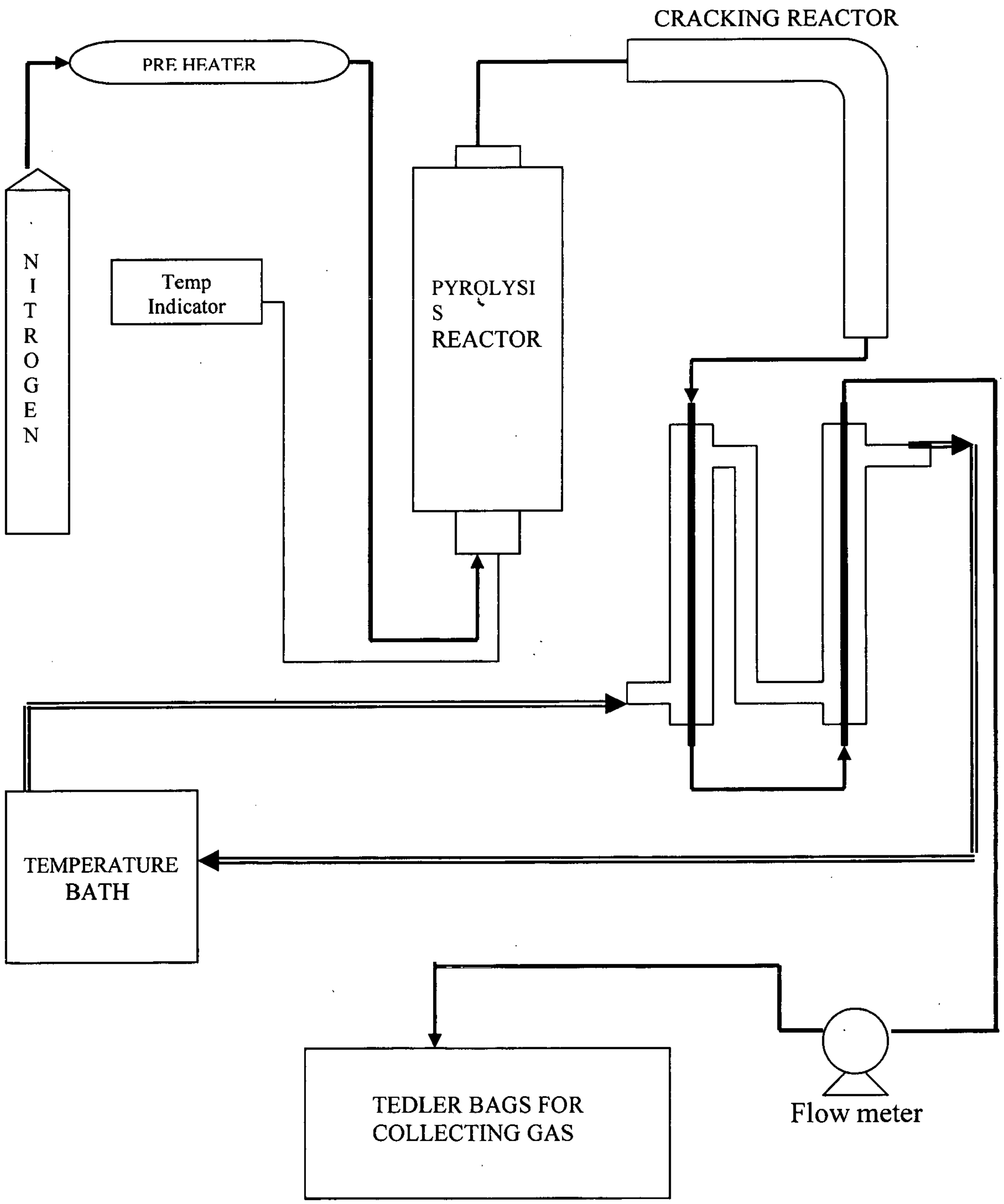


Fig 7: pyrolysis unit

5.2 Apparatus used

5.2.1 Rotameter

Rotameter was used to supply a controlled and measured sweep gas (Nitrogen) flow rate. Nitrogen is passed through the rotameter at different flow rates ranging from 50 to 200 cm^3/min. Rotameters were first calibrated using standard calibration instrument. The rotameters were also calibrated using Gas flow meter (Wet test meter). To calculate the flow rate, time was noted down for one complete cycle of Gas flow meter .The readings of calibration by gas flow meter are shown in fig-6.12

5.2.2 Preheater

The carrier gas entering the reactor was passed through the preheater to raise the temperature of the gas. The temperature of the preheater was maintained at 500 – 530 ^{0}C and was measured with the help of pyrometer. Preheater was made up of stainless steel and is 50 in. long and 0.4 in. internal diameter. The heat was provided with the help of heating coil, connected to the dimerstat.

5.2.3 Thermocouples

The thermocouples were used to measure temperature at the reactor skin and inside the reactor i.e. center and top of the reactor. Pyrometer was used to measure the temperature at the skin of the preheater. The thermocouples were calibrated with the help of thermometer.

5.2.4 Gas flow meter (Wet test meter)

Gas flow meter was used to measure the amount and rate of gas flowing out of the reactor. It was also used to measure the rate at which the gas was coming out of the reactor. The gases coming out of the reactor include nitrogen and gases produced during the reaction of pyrolysis.

5.2.5 Condenser

Condensers were used to condense the condensable gases produced during the pyrolysis. Subzero temperature is required to condense the gases.

5.2.6 Receiver

The liquid product formed during the reaction of pyrolysis was collected at the bottom of the receiver.

5.2.7 Cold Traps

Two ice traps were connected after the condenser, to condense the gases, which escape through the condenser during the pyrolysis. The temperature of the traps was maintained at about 0 ^{0}C with the help of ice.

5.3 Characterization of raw feed

5.3.1 Pretreatment of the Biomass:

(i) Biomass sample was analyzed for moisture content, calorific value, metal contents, etc.

(ii) The bulk biomass was separated into three mesh sizes by sieving using meshes of different sizes. Three mesh sizes taken were -6 +8, -8 +12, and –12 +16.

(iii) Then a known amount of the biomass was taken and was dried in the air oven till it acquired a constant weight.

(iv) During this process of drying biomass was kept in the oven for one hour duration and cooled in the desiccators and then were weighed. This process was continued till it acquired the constant weight

Once it had acquired the constant weight it was ready for to be fed into the reactor

5.4 Component analysis of biomass-procedure

5.4.1 Analysis of moisture content

Some sample of biomass of (-60) mesh was weighed. It was dried in the oven at around 80^0C for 2 hrs. The sample was cooled in desiccator and then weighed. This procedure was continued till the constant weight was obtained. After getting the constant weight, then moisture was calculated as:

$$\text{Moisture content (Ad)} = \frac{\text{Initial weight of Biomass- Wt. of Biomass after drying}}{\text{Initial Wt. of Biomass}} \text{x100}$$

5.4.2 Analysis of extractive

Procedure

Some amount (G_0, gms) of dried biomass was taken in a thimble. It was put in the Sox let apparatus. Benzene/ethanol mixture was taken in the volume ratio of 2:1. Biomass was leached at constant temperature for 3 hours. After this process kept this residue in Petri dish at room temperature. Then residue was air dried in an oven at 105-110^0 C to a constant weight. The residue was cooled in desiccators and weighed (G_1, gm). The extractive weight was calculated as:

$$W_1 \text{ (Wt \%)} = \frac{(G_0 - G_1)}{G_0} \text{x100}$$

5.4.3 Analysis of Hemi cellulose:

Procedure

Known amount (G_1) of residue obtained from extractive analysis was taken in a flask. Prepared 150 ml NaOH solution (20gms/Lit) and added it to the flask. The mixture was boiled for 3.5 hrs with recycled distilled water.

Filter and wash the residue till no more Na+, and it was dried to constant weight. The residue was then cooled to room temperature in desiccator and weighted (G_2). The hemi cellulose wt% was calculated as:

$$W_2\ (\text{Wt}\ \%) = \frac{(G_1 - G_2)}{G_1} \times 100$$

5.4.4 Analysis of Lignin

Put about 1gm of residue after extractives analysis as above in a weighted flask and dry it to a constant weight. The sample was then cooled in desiccators and weighted (G_3, gms). Slowly pour 30 ml of sulphuric acid (72%) in to sample and keep the mixture at $8\text{-}15^0$ C for 24 hours. Dilute the mixture with 300 ml of distilled water. The sample was boiled for 1 hr with recycled distilled water. After cooling and filtration the residue was washed until there was no more sulphate ion in the filtrate. The residue was then dried to a constant weight. Cooled to room temperature in desiccators and weighted (G_4, gm). The lignin wt% was then calculated as:

$$W_3\ (\text{wt}\ \%) = [G_4 (1 - W_1/100)] \times 100$$

5.4.5 Analysis of cellulose

The cellulose was calculated as:

$$W_4\ (\text{wt}\ \%) = 100 - (Ad + W_1 + W_2 + W_3)$$

5.4.6 Trace Metal analysis

Trace metal analysis of sieved Jatropha curcas were performed using atomic emission spectrometer (Model No: PS-3000 UV, IUPAES (Inductively Coupled Plasma Atomic Emission Spectroscopy))

5.5 Catalyst preparation

To perform the process of biomass conversion to hydrogen different catalysts can be used. The catalyst to be used is a Ni based aluminum catalyst with different weight percent. Some of the catalysts prepared are:

- **i. 5% NiO/Al_2O_3**
- **ii. 8% NiO/Al_2O_3**
- **iii. 12% NiO/Al_2O_3**
- **iv. 15% NiO/Al_2O_3**

5.5.1 Raw material

For the production of catalyst raw material needed is pural pseudo bohemite, and Ni $(NO_3)6H_2O$.

5.5.2 Equipment used

Caclinator, 5ml Beaker, Magnetic stirrer bath and Dryer

5.5.3. Procedure:

A known amount of Pural Pseudo Bohemite was taken in a tray and was calcinated at 500°C for two hours. The product obtained was γ-Al_2O_3. This has the surface area of $230m^2/gm$ and power volume of 0.5cc/gm (water retaining capacity). As it was seen that NiO does not exist in the pure form but as in the form of Ni $(NO_3)6H_2O$.

Appropriate amount of Ni $(NO_3)6H_2O$ was taken for the preparation of catalyst. The appropriate calculations for the required amount of NiO for the preparation of each type of catalyst are:

Amount of catalyst to be prepared= 10gm

Weight % of NiO required for the specific type= ‘x’ wt%

Amount of Al_2O_3 taken= (100-x) wt%

For 10 gm of the catalyst NiO present is given by

$$[x / (100-x)]10 = \text{'y' gm},$$

This implies, 'y' gm of NiO is needed for the preparation of x wt % catalyst. This 'y' gm will correspond to z amount of Ni $(NO_3)6H_2O$ implying that 'z' moles of Ni (NO3)6H2O will give x wt % of NiO required for the specific type of catalyst.

'z' gm of $Ni(NO_3)6H_2O$ was dissolved in 5ml of distilled water. This solution was then added to γ Al_2O_3. The product was dried at 110°C for six hours followed by calcination at 500oc for four hours. Same procedure was repeated for the other types.

5.5 Experimental procedure

Pyrolysis of biomass material was conducted in a batch pyrolysis assembly as shown in Fig., which can contain up to 600 g of biomass. Generally speaking, the pyrolysis assembly consists of three parts: reactor part (pyrolysis reactor, cracking reactor and heating furnace), condenser and purification part (condenser I and II) and gas storage part (Tedlar bag). The pyrolysis reactor is a cylindrical configuration made of stainless steel (total height,900 mm; 68.77mm i.d.) and normally is immersed in an externally heated furnace (431.48mm i.d.) lined with insulated materials of silica–alumna wool.

In the pyrolysis experiments, two different sizes of **JATROPHA CURCAS** (mesh no. -6+8,–8+12 and –12+16) were used. The Jatropha curcas was filled in the reactor up to a height of 17” from the mesh. Nitrogen flow rate was controlled and measured by the rotameter. The nitrogen flow rate of 50, 100, 150 cm^3/min. were employed. Nitrogen was preheated up to a temperature of 500 – 530 ^{0}C and fed to the top of the reactor. The reactor was heated at a constant heating rate of 10 ^{0} C/min, under a nitrogen atmosphere to a final temperature of 400, 500 and 600^{0}C.

The thickness of the insulating materials is around 323.01 mm. The outlet of the pyrolysis reactor is connected to a cracking reactor via a connecting tube, and thus the volatile phase leaving the pyrolysis reactor is subjected to an additional cracking reaction and afterwards flows into a condenser. The condenser consists of two stages, one hot water (condenser I) and the other the mixed ice/water (condenser II). Most of the water entrained by the pyrolysis gas and a little still uncondensed tarry component are further removed there in. The gas exiting from the condenser first is introduced into a tedlar bag, followed by a gas vent.

The connecting tube before the condenser is always well insulated to prevent the tarry components from condensing. The connecting tube between the pyrolysis reactor and cracking reactor and between the cracking reactor and condenser I is made of high temperature (800^{0}C) resistant material, while the rest is made of middle temperature (300–400 ^{0}C) resistant Teflon. The capacity of the external heating furnace is, at first 4 kW and then was changed to 8 kW in order to shorten the operational time. Of this, 2 kW is set to run the cracking reactor. Nitrogen is passed through a flow meter, serving as the purge gas and protective gas to avoid coking occurring on the surface of the reactor before and after operation. The reactor temperature is measured by thermocouples welded onto its inner wall which can be automatically switched on or off by a temperature controlled program.

Before an experiment, a certain amount of biomass materials is placed into the batch fixed bed reactor. The effective occupation of the biomass used is around 15% of the reactor capacity. This treatment would lead to sufficient residence time of the volatiles produced. At the 80% axial height of the reactor, multi-layer wire netting is installed in order to increase the average temperature of the volatiles. Above the wire netting, a thin layer of glass wool is used to support a certain thickness of catalyst powder.

After this work has been done, the N_2 flow is activated to purge the air retained in the reactor. Following this, the pyrolysis then really starts, that is, the N2 flow is now reduced to a very small amount (<200 ml/min), and afterwards, the pyrolysis reactor is inserted into the heated furnace, which has already been controlled at the desired temperature.

The biomass particles are continuously heated by the radiation of the heated furnace and finally reach the desired temperature. At the desired temperature, the biomass is kept for 20 min until no further gas obviously forms. For the experiments here, the cracking reactor is set at the temperature level of 500^0C, only for preventing condensing occurring, not for the purpose of thermally cracking the tar product. It is obvious that our experimental procedure favors the production of hydrogen rich gas due to the long residence time and high average temperature level.

The vapors formed during the pyrolysis of biomass enter the condenser after coming out of the reactor. The condensable gases condense to the liquid and the collected in the receiver. The temperature of the condenser is maintained at 15 ^{0}C. The gases are further passed through a series of ice traps maintained at 0-5 ^{0}C to condense the gases which escape through the condenser. The amount of gas going out in the atmosphere was measured by gas flow meter. At the end of every experiment, the pyrolysis residue is weighed to determine the yields, and the gas yield is calculated for most runs directly based on its measured volume and the gas components analyzed by gas chromatography.

The pyrolysis liquid is collected under special requirements and afterwards weighed. Aqueous phase and non aqueous phase were separated using Dean stark apparatus and weighed separately using balance (Model: Saritorius) up to accuracy of two digits (+-0.01 gm).

Known amount of toluene is added to the oil water mixture before charging it for water removed by Dean stark apparatus. The gas was collected in the toddler bags has been given for further characteristics. JULBO water was used to produce cooling effect in condensers made of316 Stainless steel (0.025" i.d and 1.0" o.d).

The catalysts can be placed into the pyrolysis reactor in two ways: one as mentioned above in the layer of glass wool and the other in the mix with the original biomass particles prior to the experiments.

5.6 Gas analysis

After the process of Pyrolysis, gases can be analyzed by GC using N_2 as mobile gas in a refinery gas analyzer by using chemitto, 8600 refinery gas analyzer.

CHAPTER 6

DESIGN ASPECTS

6.0 Design of Laboratory fixed bed Tubular unit for hydrogen production

Generally, the assembly of **Laboratory fixed bed Tubular reactor** consists of three parts:

1. Pyrolysis Reactor
2. Cracking Reactor
3. Heating furnace

6.1 Pyrolysis Reactor

The stainless steel tubular reactor was used which is 90 cms High x 7.1 ID. and was heated externally by an electric furnace. A wire mesh was provided at about 54 cms from the bottom of the reactor to hold the biomass in the reactor. The N_2 was purged from the bottom of the reactor at the height of 4 cms from reactor bottom. And gases leave from the top. The temperature of reactor inside and reactor skin was measured with the help of thermocouples. Three thermocouples were inserted from the bottom of the reactor to measure the temperature of the center and top of the reactor and middle of the reactor. The effective occupation of the bio mass the wall thickness of this reactor was less than the tubular reactor of smaller diameter. The reactor is shown in Fig 7. The bio mass occupied in the reactor is 15 % of the volume of the reactor.

6.1.1 Flange Design

1. All dimensions are in inches.
2. Mateial commonly used are forged steel SA 181, available also in SS and alloy steel.
3. The length of the stud bolt does not include the height of crown.
4. Bolts holes are 1/8'' inch larger than bolt diameters.
5. Flanges bored to dimension shown unless otherwise specified.
6. Flange for this pipe size taken from the ANSI B1 6.5.

Flange design for nominal pipe size 3 inches with standing 150 lb pressure (atmospheric)

Diameter of the Bore is	A	3.07 inch
Length through the hub	C	2.75 inch
Diameter of hub at point welding	E	3.5 inch.
Diameter of hub at the base	G	4.25 inch.
Outside Diameter of flange	H	7.5 inch.
Thickness of flange	J	15/16 inch.
Outside diameter of the raised face	K	5 inches.
No of holes		4
Diameter of bolts		5/8 inch
Bolt circle		6 inch
Length of bolt		3.75 inch

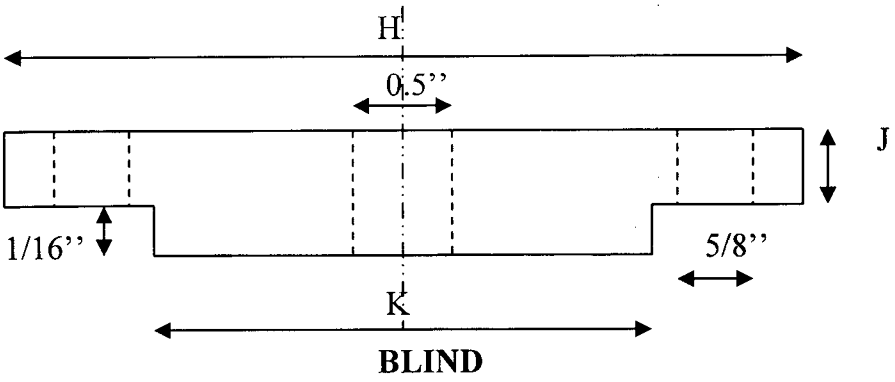
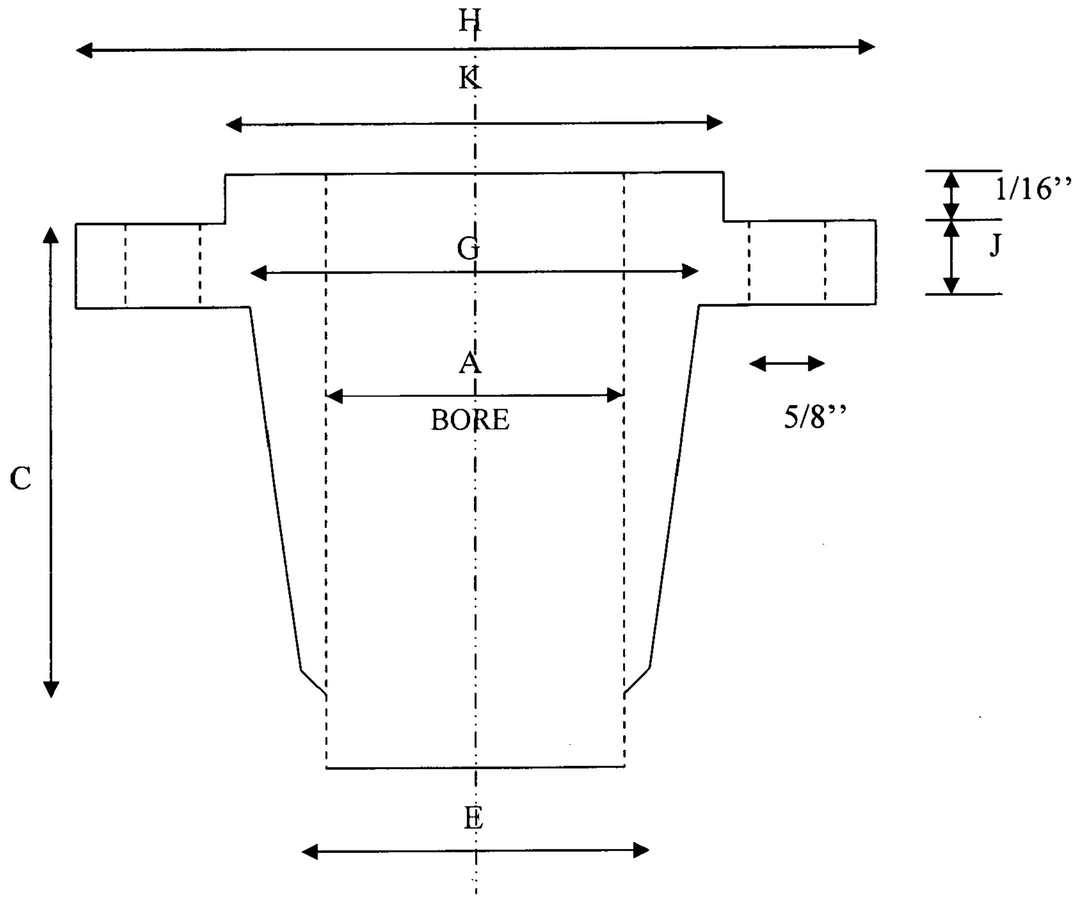


FIG 8: BLIND



WELDING NECK

Fig 9: WELDING NECK

6.1.2. Mechanical Design of laboratory scale reactor

Diameter of the pipe	7.1 cm [ID]
Length of the pipe	90 cm
Thickness of the bottom plate	0.3 cm
Thickness of the pipe	0.3 mm

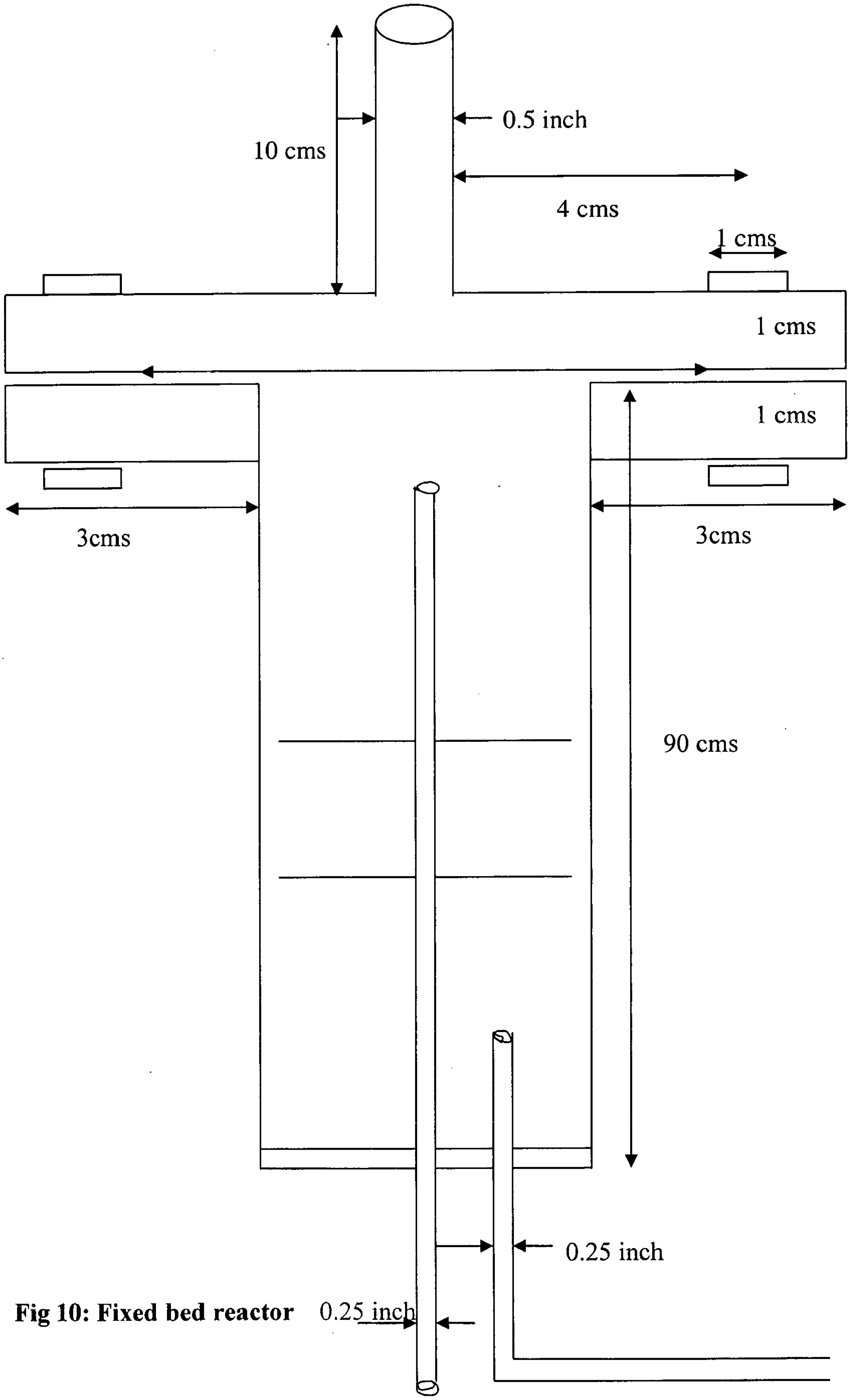


Fig 10: Fixed bed reactor

6.2 Cracking Reactor

Cracking Reactor made of stainless tube of 0.5-inch internal diameter tube of length 15 cms. Heating with temperature 500^0C (2 Kw of power) and having a thermal insulation with Asbestos insulating material.

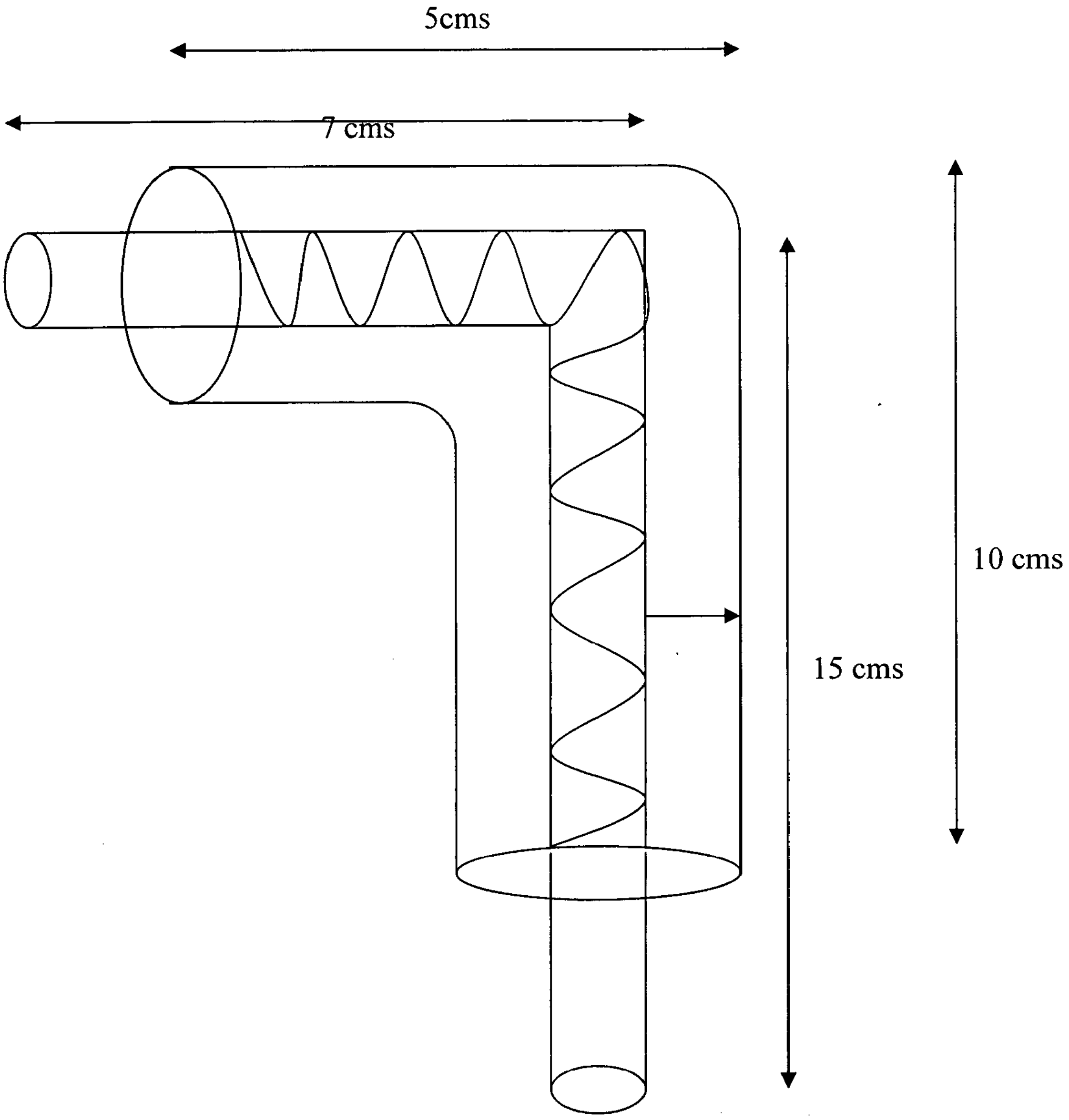


Fig 11: Cracking reactor

6.3 Heating furnace

Two heating furnaces are used for hydrogen production by pyrolysis method, one for the fixed bed reactor and another for cracking reactor.

6.3.1 Insulation Design calculation for fixed bed reactor

Consider two tubes one is Silicon tube and another one is Stainless tube each having diameters are 7.7cms, 10.8cms respectively. For requiring temperature of 900^0c at the surface of the SS tube we were giving power supply of 6Kw to the outer surface of the Silicon tube, which is concentric with the SS tube. To reduce heat losses insulation made with fire clay material.

Power supplied to Silicon tube at = 2 Kw = 2000 j/sec
Each four points

= 2000* 0.2389 cal/sec

Heat evolved in 1 sec =477.8 cal

Thermal conductivity of fire clay material = 0.77 BTU/hr.^{0}F.ft

= 9.824 E^{-4} cal/sec.cm.^{0}C

Length of the Silicon tube =100 cm

Radius of the Silicon tube,r_o =5.4 cm

Assuming the Temperature at the outer surface of the Silicon tube, T_{in} $\}$ =1100^0C

Required temperature at the outer surface of the furnace after insulation, T_{out} $= 27^0C$

$$Q = \frac{2\Pi\, k\, L\, (T_{in} - T_{out})}{\ln\, (r_{out}/r_{in})}$$

$$Q = \frac{2\Pi\, k\, L\, (T_{in} - T_{out})}{\ln\, ((r_{in}+x)/r_{in})}$$

$$\ln\, ((r_{in}+x)/r_{in}) = \frac{2\Pi\, k\, L\, (T_{in} - T_{out})}{Q}$$

$$((r_{in}+x)/r_{in}) = \text{Exp}\left\{ \frac{2\Pi\, k\, L\, (T_{in} - T_{out})}{Q} \right\}$$

$$((r_{in}+x)/r_{in}) = \text{Exp}\left\{ \frac{2*\Pi*9.824*10^{-4}*100*(1100 - 27)}{477.8} \right\}$$

$$((r_{in}+x)/r_{in}) = \exp[1.386186927]$$

$$((r_{in}+x)/r_{in}) = 3.9995702$$

$$((5.4+x)/5.4) = 3.9995702$$

$X = 16.197679$ cm

$r_0 = 21.59767955$ cm

Diameter of insulation is $D_o = 43.1953$ cm

6.3.2 Design calculation for Insulation of cracking reactor

Power supplied to SS tube at = 2 Kw = 2000 j/sec
Each four points

= 2000* 0.2389 cal/sec

Heat evolved in 1 sec =477.8 cal

Thermal conductivity of fire clay material = 0.77 BTU/hr.^{0}F.ft

= 9.824 E^{-4} cal/sec.cm.^{0}C

Length of the SS tube =15 cm

Radius of the SS tube,r_o =1.27 cm

Assuming the Temperature at the outer surface of the =700^{0}C

Required temperature at the outer surface of the furnace after insulation, T_{out} = 27^{0}C

$$Q = \frac{2\Pi k L (T_{in} - T_{out})}{\ln (r_{out}/r_{in})}$$

$$Q = \frac{2\Pi k L (T_{in} - T_{out})}{\ln ((r_{in}+x)/r_{in})}$$

$$\ln ((r_{in}+x)/r_{in}) = \frac{2\Pi k L (T_{in} - T_{out})}{Q}$$

$$((r_{in}+x)/r_{in}) = \text{Exp} \left\{ \frac{2\Pi k L (T_{in} - T_{out})}{Q} \right\}$$

$$((r_{in}+x)/r_{in}) = \text{Exp} \left\{ \frac{2*\Pi*9.824*10^{-4}*15*(700 - 27)}{477.8} \right\}$$

$$((r_{in}+x)/r_{in}) = \exp[0.13041]$$

$$((r_{in}+x)/r_{in}) = 1.1393013$$

$$((1.27+x)/1.27) = 1.1393013$$

$X = 0.1651\text{cm}$

$r_0 = 1.4351\text{cm}$

Diameter of insulation is $D_o = 2.3702\text{cm}$

CHAPTER 7

RESULTS AND DISCUSSION

7.0 RESULTS

7.1 Pretreatment of biomass:

Serial No.	Time of heating (Hr)	Biomass size -6+8	 -8+12	 -12+16	 -16
1	3	459.71	680.42	405.56	663.03
2	2	449.68	675.16	398.15	649.95
3	2	447.14	673.63	394.74	645.78
4	2	444.14	673.61	392.8	643.83
5	2	444.05	673.62	390.28	642.15
6	2	443.72	673.63	389.76	641.85
7	2	443.64	673.62	388.99	641.34
8	2	435.54		388.83	641.25
9	2	434.80		387.62	639.73
10	2	434.68		387.16	639.34
11	2	434.66		387.07	639.21
12	2	434.67		387.05	639.20
13	2			387.06	639.20

Table 19: Constant weight determination of Jatropha Curcas seed cake

Results:		
	Constant weight for the mesh size –6+8 was at	434.67gm.
	Constant weight for the mesh size –8+12 was at	673.62gm.
	Constant weight for the mesh size –12+16 was at	387.06gm.
	Constant weight for the mesh size –16 was at	639.20gm

7.2 Moisture content Results

Mesh size	Particle size (mm)	% Moisture
-6+8	2.8445	5.5%
-8+12	1.8795	.99%
-12+16	1.194	4.5%
-16	0.991	3.6%

Table 20: Moisture content of Jatropha curcas seed cake

7.3 Component analysis Results

Biomass: Jatropha curcas seed cake

7.3.1 Extractives: **1.11%**

7.3.2 Hemi cellulose: **40.0%**

7.3.3 Cellulose: **28.89%**

7.3.4 Lignin: **29.0%**

7.4 Trace metal analysis Results

Biomass: **Jatropha curcas seed cake**
Technique: **ICP-AES**
Model: **DRE, PS (3000) UV, LEEMAN LABS, INC USA**

Metal	Zn	Cr	Cd	Ni	Pb	Cu	Co
Amount (mg/L)	258.0	3.35	<1.00	6.90	4.80	38.35	1.30

Table 21: Trace metal analysis

7.5 Catalyst Preparation

Amount of Pural Pseudo Bohemite taken 10gm

Catalyst 1

1. 5% NiO/Al_2O_3

Ni $(NO_3)6H_2O$, Molecular wt = 291.03

[5/95]10 = 0.526 gm

= 0.007013 Mol NiO = 0.007013 of Ni $(NO_3)6H_2O$.

Ni $(NO_3)6H_2O$ required is = 2.0409 gm

2. **8% NiO/Al_2O_3**

Ni $(NO_3)6H_2O$, Molecular wt = 291.03

[8/92]10 = 0.869 gm

= 0.01159 Mol NiO = 0.01159 of Ni $(NO_3)6H_2O$.

Ni $(NO_3)6H_2O$ required is = 3.374 gm

3. **12% NiO/Al_2O_3**

Ni $(NO_3)6H_2O$, Molecular wt = 291.03

[12/88]10 = 1.36 gm of NiO

= 0.01818 Mol NiO = 0.01818 of Ni $(NO_3)6H_2O$.

Ni $(NO_3)6H_2O$ required is = 5.29 gm

4. 15% NiO/Al_2O_3

Ni $(NO_3)6H_2O$, Molecular wt = 291.03

[12/88]10 = 1.36 gm of NiO

=0.01818 Mol NiO = 0.01818 of Ni $(NO_3)6H_2O$.

Ni $(NO_3)6H_2O$ required is = 5.29 gm

8.0 CONCLUSIONS:

8.1 Benefits of Bio-mass

- Biomass is a renewable, potentially sustainable and relatively environmentally benign source of energy.
- A huge array of diverse materials frequently stereo chemically defined is available from the biomass giving the user many new structural features to exploit.
- Increased use of biomass would extend the lifetime of diminishing crude oil supplies.
- The natural decomposition of biomass produces methane, which is about twenty times more active as a greenhouse gas than carbon dioxide.
- Biomass fuels have negligible sulfur content and, therefore, do not contribute to sulfur dioxide emissions, which causes acid rain.
- The combustion of biomass produces less ash than coal combustion, and the ash produced can be used as a soil additive on farm targets.
- The combustion of agricultural and forestry residues and MSW for energy production is an effective use of waste products that reduces the significant problem of waste disposal, particularly in municipal areas.
- Biomass is a domestic resource, which is not subject to world price fluctuations or the supply uncertainties of imported fuels. In developing countries in particular, the use of liquid biofuels, such as biodiesel and ethanol, reduces the economic pressures of importing petroleum products.
- Biomass provides a clean, renewable energy source that could improve our environment, economy, and energy securities.
- The use of biomass could be a way to mitigate the build up of carbon dioxide in the atmosphere because of use of biomass as a feedstock results in no net increase in the atmospheric carbon dioxide level.
- Biomass is more flexible feedstock than the crude oil.

8.2 Constraints

- In nature, biomass is not concentrated, and so, the use of naturally occurring biomass requires transportation, which increases the cost.
- Biomass has low bulk density, which makes transportation and handling difficult and costly.
- The incomplete combustion of fuel wood produces organic particulate matter, carbon dioxide and other organic gases. The health impact of air pollution inside buildings is a significant problem in developing countries, where fuel wood is burnt inefficiently in open fires for domestic cooking and space heating.

- There is the potential for widespread use of natural forests to cause deforestation and localized fuel wood scarcity.
- There is a potential conflict over the use of land and water resources for biomass energy and other uses such as food production.
- Some biomass applications are not fully competitive at this stage. However the economics of biomass energy production are improving and the growing concern about greenhouse gas emissions is making biomass energy more attractive.
- The production and processing of biomass can involve significant energy input, such as fuel for agricultural vehicles and fertilizers, resulting in a poor energy balance.
- The biofuels usually have only a modest thermal content compared with fossil fuels.
- The combustion efficiency of the biomass fuel is low.
- Corrosion deposit on the heat transfer surface due to the high alkali and chloride content.
- High degree of maintenance because of the impure gases.
- High moisture content, low bulk density and produce highly erosive ash.

Further research

Hydrogen is currently more expensive than conventional energy sources. The production efficiency (the amount of gaseous energy recovery from the feedstock used to produce hydrogen) must be improved and an infrastructure for efficiently transporting and distributing hydrogen is to be developed. There are different technologies presently being practiced to produce hydrogen economically from biomass. However, it is too early to predict which of these biomass-conversion technologies will be ultimately successful. Biohydrogen technology will play a major role in future because it can utilize the renewable sources of energy.

To find the optimal condition for the production of Hydrogen further study is needed.

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