# A REVIEW OF NUCLEAR SOURCES OF NON-FOSSIL CHEMICAL FUELS

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## Summary

Energy derived from nuclear sources can be utilized either in the form of high energy radiation, thermal energy or electrical energy. Each of these energy forms can be employed to produce non-fossil chemical fuels by transformation of available non-fossil substances. As a general definition, available non-fossil fuel substances are all resources other than coal, petroleum, or natural gas. Thus the substances that can serve as raw materials for nuclear energy conversion to non-fossil chemical fuels, are basically the substances found in water, air, and minerals.

High energy radiation from nuclear fission can be utilized either directly as fission fragment energy in a chemonuclear reactor or indirectly as neutron, gamma, and beta energy from isotopic sources. Fission fragment energy is actually the only radiation energy source that can be generated in sufficient quantity and at low enough cost of be considered for production of fuels. The two basic fuels that can be generated are hydrogen from water and carbon dioxide, and carbon monoxide from carbon dioxide. The hydrogen and carbon monoxide can be used as fuels or can be subsequently converted to high BTU gas or other liquid hydrocarbons. The main difficulties with fission fragment chemonuclear systems are obtaining sufficiently high yields of fuel gases and demonstrating that a fuel essentially free of radioactive fission fragments can be produced.

Thermal energy from nuclear fission in the form of steam or a high temperature gas stream such as helium can, conceivably, be used to crack water to hydrogen and carbon dioxide to carbon monoxide. Carbon dioxide can be derived from thermal de-

composition of limestone or by extraction from the atmosphere. However, the temperatures are too high to allow safe operation of the nuclear reactors required for these processes with the materials of construction generally available. Nuclear thermal energy can be used to preheat streams and makeup heat balances and to gasify coal and thus, although not strictly a source of non-fossil chemical fuel serves to partially extend the supply of non-fossil fuel.

Nuclear based electrical energy derived from standard steam and gas power cycles or from more advanced cycles such as MHD can be utilized to power electrolytic cells or electric discharges. In electrolytic cells, water can be used as a primary source of fuel or converted to a number of other fuels including ammonia, methanol, methane, hydrazine, acetylene, and others. The electric discharge can also be employed to decompose water and carbon dioxide, however, this process is usually less efficient than electrolysis. Aluminum, magnesium, and other reactive metals can be electrochemically produced and used as fuels.

Probably the most practical source of nuclear based non-fossil chemical fuels is the nuclear fission reactor powered electrolytic decomposition of water to hydrogen.

Another class of non-fossil fuels are the boranes, and silanes, These can be derived from hydrogen, borax and silica.

In the longer term future it is conceivable that fusion energy will replace fission as a nuclear source. Generally fusion could be applied in similar fashion to the above processed to produce non-fossil chemical fuels.

## I. Introduction

Probably the best way to set the ground rules for this Symposium is to define what a non-fossil chemical fuel is. Very generally a fuel is a substance which when made to react releases energy in one form or another. A chemical fuel is a fuel which releases energy when the fuel is made to undergo a chemical transformation. A non-fossil chemical fuel is a chemical fuel which is derived from non-fossil substances. Non-fossil substances are generally all substances other than coal, petroleum or natural gas.

Some of the reasons for considering non-fossil chemical fuels are as follows:

1. Fossil fuels are being depleted at an increasingly rapid rate. It is estimated that by the end of this century the U.S. natural gas supplies will be largely exhausted and that less than 10% of the electrical power generating capacity will be supplied by oil and gas[10]. The major sources of fuel for electrical power will be derived from coal and nuclear. Oil and gas will be mainly used for fueling mobile engines. Alternate sources of chemical fuels would thus conserve our fossil fuel reserves.

2. Fossil fuel in the form of natrual gas and oil also serve the chemical industry for non-fuel purposes. Thus non-fossil chemical fuels would aid the chemical industry in extending its reserved of raw materials.

3. Non-fossil chemical fuels would add to the supply of low pollution fuels. Natural gas and some oil reserves are presently premium sources of low pollution electrical power.

4. Non-fossil chemical fuels can act as energy storage systems.

5. It is also possible that more efficient fuels can be produced from non-fossil sources.

In order to produce a chemical fuel from non-fossil substances, energy is required in the transformation process. Adhering strictly to definition, this energy must be derived from non-fossil fuels. This restricts the energy sources to nuclear, hydroelectric, solar, geothermal, tidal, and meteorological. From the point of view of long term availability and intensity, nuclear energy will be the main viable non-fossil energy source. Nuclear energy at present is derived from fissionable fuel. In the future, nuclear fusion will also be a major energy source.

In order for non-fossil substances to be a major source of raw material for non-fossil chemical fuels the substances must be readily available and abundant in supply. The raw material sources, essentially reduce to the following:

1. Water - $H_2O$
2. Air $CO_2$- $O_2$, $N_2$ and Ar
3. Minerals - limestone, dolomite, bauxite, borax, and silica.
4. Waste Materials.

Without necessarily going into the actual quantity of $CO_2$ existing in the atmosphere, the almost 600 million tons of coal produced and consumed in the United States annually is released to the atmosphere as carbon dioxide. There is thus no question that there is an abundant $CO_2$ supply in the atmosphere. It is an engineering and economics problem to recover the $CO_2$ by some process for example, either absorption or by cryogenic separation. A benefit of a $CO_2$ recovery process might be to maintain the $CO_2$ balance in the atmosphere and avoid the possible "greenhouse effect" of increasing the earth's temperature by infra-red absorption due to increasing $CO_2$ concentrations.

The reason waste materials are included in the above listing is that there is a mounting supply and although much of the waste is derived from fossil fuel, the production of chemical fuel from waste is not a direct derivation from fossil fuel. For example part of the $CO_2$ in the atmosphere is derived from fossil fuel and it becomes available as a non-fossil source of chemical fuel.

Other properties that can be ascribed to non-fossil chemical fuels are:

1. Storable
2. Transportable
3. Easily utilized in conventional and non-conventional engines.

Fossil fuels are essentially reduced chemical substances which when oxidized in the atmosphere yield exothermic reactions which is the basis of the fuel cycle. Several prime reactions and energy releases are as follows:

| | $\Delta H_{298.2}$ Kcal/mol |
|---|---|
| $C_{(s)} + O_{2\,(g)} = CO_{2\,(g)}$ | -94.0 |
| $H_{2\,(g)} + \frac{1}{2}O_{2\,(g)} = H_2O_{(\ell)}$ | -67.9 |
| $C_nH_{2n+2} = (3/2n + 1/2)O_2 = nCO_2 + (n+1)H_2O$ | |

To produce non-fossil fuels, nuclear energy can be used to reverse this thermodynamic cycle and essentially the energy is converted and stored in the form of chemical energy in the chemical fuels. In another sense, nuclear energy is used to recycle products formed in the utilization of fossil fuels.

Energy derived from nuclear sources can be utilized either in the form of high energy radiation, thermal energy or electrical energy as discussed in the following.

## Chemonuclear Reactors

High energy radiation from nuclear fission can be utilized either directly as fission fragment energy in a chemonuclear reactor or indirectly as neutron, gamma and beta energy from isotopic sources. Fission fragment energy containing 85% of the energy released in fission is actually the only radiation energy source that can be generated in sufficient quantity as at low enough cost to be considered for production of fuels. The two basic chemical fuels that can be generated are hydrogen from water and carbon monoxide from carbon dioxide. The following table indicates the maximum radiation yield (G values in molecules/100 ev) and efficiency of conversion for these two systems[3].

Table 1

| Reaction | $\Delta H_{298.2}$ Kcal/mol | G values $G_{max}$ | $G_{exp}$ | Energy E Kwh(t)/lb | Thermal efficiency % |
|---|---|---|---|---|---|
| $H_2O_{(g)} = H_{2(g)} + \frac{1}{2}O_{2(g)}$ | +57.9 | 39.9 | 6 | 101.5 | 15.0 |
| $CO_{2(g)} = CO_{(g)} + \frac{1}{2}O_{2(g)}$ | +67.6 | 34.1 | 10 | 4.3 | 29.4 |

Because the fuel gases are generated together, separation from the oxygen is required. Furthermore, since the thermal efficiency is not very high, attempts are made to utilize the excess thermal energy for the generation of electrical power. However, upper temperature limits must be imposed to prevent back reactions. This could act as a restriction for generating power in multi-purpose chemonuclear reactors. The hydrogen and the CO can be converted by means of the water gas reactions to gaseous or liquid hydrocarbon fuel.

| Reaction | $\Delta H_{298.2}$ Kcal/mol |
|---|---|
| $CO_{(g)} + H_2O_{(g)} = CO_{2(g)} + H_{2(g)}$ | -9.7 |
| $2H_{2(g)} + CO_{(g)} = CH_{4(g)} + H_2O_{(g)}$ | -49.4 |

The source of $CO_2$ could either come from the atmosphere which has an abundant supply although it is in relatively low concentrations (0.03% by volume). $CO_2$ can also be derived from the calcination of limestone.

$$CaCO_3 = CaO + CO_2 \qquad \Delta H_{298.2} = 43.7 \text{ Kcal/mol}$$

A flow sheet of a chemonuclear process for the synthesis of CO and subsequently hydrogen is shown in Figure 1.

The main difficulties with fission fragment chemonuclear systems are obtaining sufficiently high yields of fuel gases and demonstrating that a fuel essentially free of radioactive fission fragments can be produced. The development of chemonuclear reactors progressed to the point of the installation of an in-pile research loop into the Brookhaven Graphite Research Reactor.(3) Unfortunately the development was interrupted due to a reduction in funds for maintaining operation of the research reactor. Potential economic feasibility was indicated assuming the technological problems were solved.

Thermal Energy from Nuclear Reactors

Conventional nuclear fission reactors usually have clad fuel elements so that the fission fragments are slowed down and remain in the solid elements. The high intensity energy in the fragments is degraded to heat and the temperature of the fuel elements rise. This thermal energy can be used to carry out chemical reactions. In water type reactors, both of the pressurized or boiling water type, the fuel element cladding materials are usually stainless steel. For long life of the elements in the reactor, the temperature of the steam generated in the reactor is usually limited to $\approx 575^{\circ}F$ and 1000 psi pressure.

In the near term future it is expected that the liquid metal fast breeder reactors will take over a large part of the nuclear power economy. These reactors are expected to operate at a higher temperature in the order of $1200-1400^{\circ}F$. These temperatures are too low to supply energy for producing non-fossil chemical fuels either by decomposition of water or carbon dioxide or by gasification reactions.

The thermal decomposition of water requires temperatures in the order of $5000^{\circ}F$ or more to yield over 10% conversion to hydrogen. There are no reliable materials of construction for nuclear reactors that could achieve these thermal conditions. The highest temperature experimental reactors developed were for gas turbine conditions in the aircraft nuclear propulsion program. The materials that were being considered were of the refractory metal variety including, rhodium and tungsten. However, they were not expected to generate high temperature gas streams much above approximately $3000^{\circ}F$. The ultra-high temperature reactor experiment at Los Alamos (UHTREX) was a molten plutonium reactor experiment and was intended to operate below $3000^{\circ}F$.

It appears possible to carry out gasification reactions using nuclear heat. Although strictly not a source of non-fossil chemical fule, because the gasification reactions are endothermic, the nuclear heat can be considered as being converted to non-fossil chemical fuel in a hybrid system.

The coal gasification reactions are as follows:

| | $\Delta H_{298.2}$ | Reaction Temperature |
|---|---|---|
| $C_{(s)} + H_2O_{(c)} = CO_{(g)} + H_{2(g)}$ | +41.5 | 1600°F |
| $C_{(s)} + CO_{2(g)} = 2CO_{(g)}$ | 41.3 | 1800°F |

The reactions are endothermic and require energy input to the system.

By means of the water has shift reaction and the methanation reaction, high BTU pipe line gas can be produced.

| | $\Delta H_{298.2}$ | Reaction Temperature |
|---|---|---|
| $CO_{(g)} + H_2O_{(g)} = H_{2(g)} + CO_{2(g)}$ | -9.7 | |
| $3H_{2(g)} + CO_{(g)} = CH_{4(g)} + H_2O_{(g)}$ | -49.4 | 700°F |
| $C_{(s)} + 2H_{2(g)} = CH_{4(g)}$ | -17.9 | 1000°F |

These are exothermic reactions and usually do not require any external source of energy.

Normally the endothermic heat of the gasification reaction is supplied internally by combustion of additional amounts of coal. In order to prevent dilution of the gases with nitrogen from the atmosphere, pure oxygen is used to react with the coal. By using nuclear heat, oxygen would not be required. From an overall heat balance an equivanent of approximately 30% of the fuel gas would be generated from the non-fossil nuclear fuel source.

Another significant source of non-fossil chemical fuel is the solid waste generated in either urban or agricultural communities. For example, urban wastes contain up to 70% combustible material and usually have heating values ranging in the order of 4000-5000 BTU/lb. Solid waste can also act as a source of carbon and hydrogen in gasification reactions analogous to the coal reactions given above.

The high temperature gas cooled reactors (HTGR) which are cooled with helium can generate gas temperatures in the order of 1600°F. The high temperature helium stream can be used to indirectly heat the coal gasification reactor. The fuel elements are made of graphite clad uranium carbide. It was recently announced(9) that a study of this system is being initiated. The heat transfer material in the gasification reactor is a critical factor in the practability of such a system.

Table 2 lists a summary of the temperature conditions for different power reactors.

Table 2

Temperature Conditions for
Different Types of Nuclear Reactors

| Reactor type | Fuel element | Coolant | Maximum Coolant Temperature |
|---|---|---|---|
| Bioling Water BWR | st. st. | $H_2O$ | 575°F |
| Pressurized Water PWR | st. st. | $H_2O$ | 575°F |
| LMFBR Reactor | Zirconium | Na | 1000°F |
| High Temperature Gas Cooled Reactor | Graphite | He | 1700°F |
| Ultra High Temperature Reactor Experiment UHTREX | Molten Pu | | 3000°F |
| Aircraft Nuclear Propulsion Reactor | Tungsten, Rhodium | Air | 3000°F |

Nuclear heat can also be used to make up heat balances for hybrid power systems using coal gasification in conjunction with magnetohydrodynamic power generation.(5) This also can be considered from the point of view of extending the gas supply using nuclear.

Another place in the non-fossil fuel scheme where nuclear heat can be used is in the calcination of limestone for the generation of $CO_2$, a source of carbon for hydrocarbon fuels. The reaction takes place at approximately 1500°F and the endothermic heat of reaction is as follows:

| | $\Delta H_{298.2}$ Kcal/mol |
|---|---|
| $CaCO_{3\,(s)} = CaO_{(s)} + CO_{2\,(g)}$ | -43.7 |

Electrical Energy from Nuclear Reactors

The primary purpose for developing nuclear reactors is to generate electrical power. Usually the closed steam cycle (Rankine) with a turbogenerator is used to produce A.C. electrical power. The heat is transferred from the reactor to the steam either by water, gas or liquid metal heat transfer coolants. The electrical power can be conditioned for use as D.C. power in electrochemical cells to electrolytically decompose water to hydrogen and oxygen. The hydrogen can either be used as a primary source of fuel or can be converted to a number of other fuels including ammonia, methanol, methane, hydrazine, acetylene, and other hydrocarbon fuels.

For producing high BTU pipe line gas by use of nuclear electric power the sequence of reactions are as follows.

| | |
|---|---|
| Electrolytic Decomposition | $H_2O_{(\ell)} = H_{2\,(g)} + 1/2O_{2\,(g)}$ |
| $CO_2$ Production from air or | Air $(CO_2) = CO_{2\,(g)}$ |
| calcination | $CaCO_{3\,(s)} = CaO_{(s)} + CO_{2\,(g)}$ |
| Reverse shift conversion | $H_{2\,(g)} + CO_{2\,(g)} = CO_{(g)} + H_2O_{(g)}$ |
| Methanation | $3H_{2\,(g)} + CO_{(g)} = CH_{4\,(g)} + H_2O_{(g)}$ |

The coupling of nuclear power reactors with electrochemical cells has been discussed previously under the nomenclature of electrochemonuclear systems.[7] They also form the basis for the multipurpose agro-industrial complex and the Nuplex[4,7] which have been widely discussed and recently studied in detail.

The electrochemical decomposition of water has been accomplished in well developed low pressure atmospheric cells at efficiencies of 60 to 70%. The more recently developed high pressure cells which operate at pressures of 30 atmospheres or above can develop efficiencies of 85% as listed in Table 3.

Table 3

The Electrochemical Decomposition of Water

| Cell Efficiency | KWH/lb $H_2$ | KWH/MSCF $H_2$ |
|---|---|---|
| 100% theoretical | 17.8 | 94.5 |
| 85% hi-pressure | 21.0 | 112.0 |
| 65% low-pressure | 27.4 | 145.5 |

A flow sheet of the process steps for the synthesis of non-fossil high BTU methane pipeline gas is shown in Figure 2. The economics of the process depends strongly on the cost of electrical power from large nuclear reactors and on the utilization of by-product oxygen. In the scheme in Figure 2, the oxygen is used for gasification of coal in an adjoining unit to add to the production of methane fuel. A host of other uses for by-product oxygen have been suggested such as in the basic oxygen furnace for production of steel.[(1)]

To illustrate the economics of such a process, for a very large 250 million cubic feet per day high BTU methane fuel gas plant, an electrical power consumption of 4670 MW would be required to produce the necessary hydrogen to convert the $CO_2$ to $CH_4$. If power from nuclear units costs 3 mils/Kwh, the cost of electrical power for hydrogen production is \$0.34/MSCF $H_2$. The depreciation on the electrolytic cell plant could add another 22% to the cost, so that the electrical cost really dominates the production cost for nuclear based electrolytic hydrogen.[(4)] Since 4 moles of hydrogen are required to combine with 1 mole of $CO_2$ to produce $CH_4$ in the above non-fossil process scheme the cost of product methane production would be \$0.67/MSCF. If a credit of \$6/ton of oxygen can be obtained then a credit of \$0.50/MSCF methane results. Today very large scale oxygen plants might produce oxygen for as low as \$3/ton. Thus combining the lowest nuclear by-product power in the future with the lowest conventional oxygen credit could bring the major fraction of the methane production cost down to \$0.42/MSCF. This compares to natural gas today which is rising above \$0.40/MSCF. Gas from projected coal gasification plants is being estimated at \$0.50 to \$0.60 MSCF. Of course, today the above estimates are probably highly optimistic, however, the possibility of an economically competitive situation may exist in the future. This depends on a combination of factors, including the logistics of multipurpose process systems and the supply of natural gas. A continuous examination of these factors could uncover an economically viable application of nuclear based electrolytic systems.

Other fuels which can be produced from hydrogen and $CO_2$ either from the atmosphere[2] or by calcining limestone are listed in Table 4.

Table 4

Fuels Which Can Be Produced from $H_2$ and $CO_2$

| Reaction | Fuel |
| --- | --- |
| $H_2O = H_2 + \frac{1}{2}O_2$ | Hydrogen |
| $3H_2 + N_2 = 2NH_3$ | Ammonia |
| $CO_2 + 3H_2 = CH_3OH + H_2O$ | Methanol[2] |
| $2CH_4 = C_2H_2 + 3H_2$ | Acetylene |
| $2NH_3 = N_2H_4 + H_2$ | Hydrazine |

Electrical power from nuclear reactors can also be used in electric discharge processes to decompose water or carbon dioxide. Electric discharge processes are usually less efficient than electrochemical processes. An efficient process for production of acetylene from calcium carbide produced by electric furnace reaction of carbon with lime is a relatively efficient reaction.

| | $\Delta H_{298.2}$ Kcal/mol |
| --- | --- |
| $CaO_{(s)} + 3C_{(s)} = CaC_{2\,(s)} + CO_{(g)}$ | +118.3 |
| $CaC_{2\,(s)} + 2H_2O_{(\ell)} = C_2H_{2\,(g)} + Ca(OH)_{2\,(aq)}$ | - 42.7 |

The use of nuclear electric power for the electric furnace production of carbide and subsequently acetylene can be viewed in the same light as the use of nuclear heat in the gasification of coal. With the aid of coal, nuclear based electrical power can be converted to additional non-fossil chemical fuel.

Nuclear electric power can be used to electrochemically produce aluminum and magnesium. These reactive metals can be made to burn as solid fuel and have indeed been used as such in specially designed burners. Also hydrogen can be made to burn with halogens such as chlorine to yield energy. Other non-fossil fuels such as the boranes which are boron-hydrogen compounds and the silanes which are silicon-hydrogen compounds can be produced from non-fossil natural resources with the aid of nuclear energy. However, all these types of fuels cannot be easily burned in conventional engines and in addition cause severe materials corrosion problems and introduce excessive pollutants into the environment.

## Nuclear Fusion Reactors

In the longer term future it is conceivable that nuclear fusion reactions utilizing deuterium as fuel will replace fission as the prime nuclear energy source. Generally speaking fusion could be applied in a fashion similar to fission as shown in the processes mentioned above for producing non-fossil chemical fuels. Probably the most practical method of utilizing nuclear fusion for production of non-fossil chemical fuel is to use the electrical energy to decompose water for hydrogen and oxygen production and these in turn can be used as such or converted to other chemical fuels.

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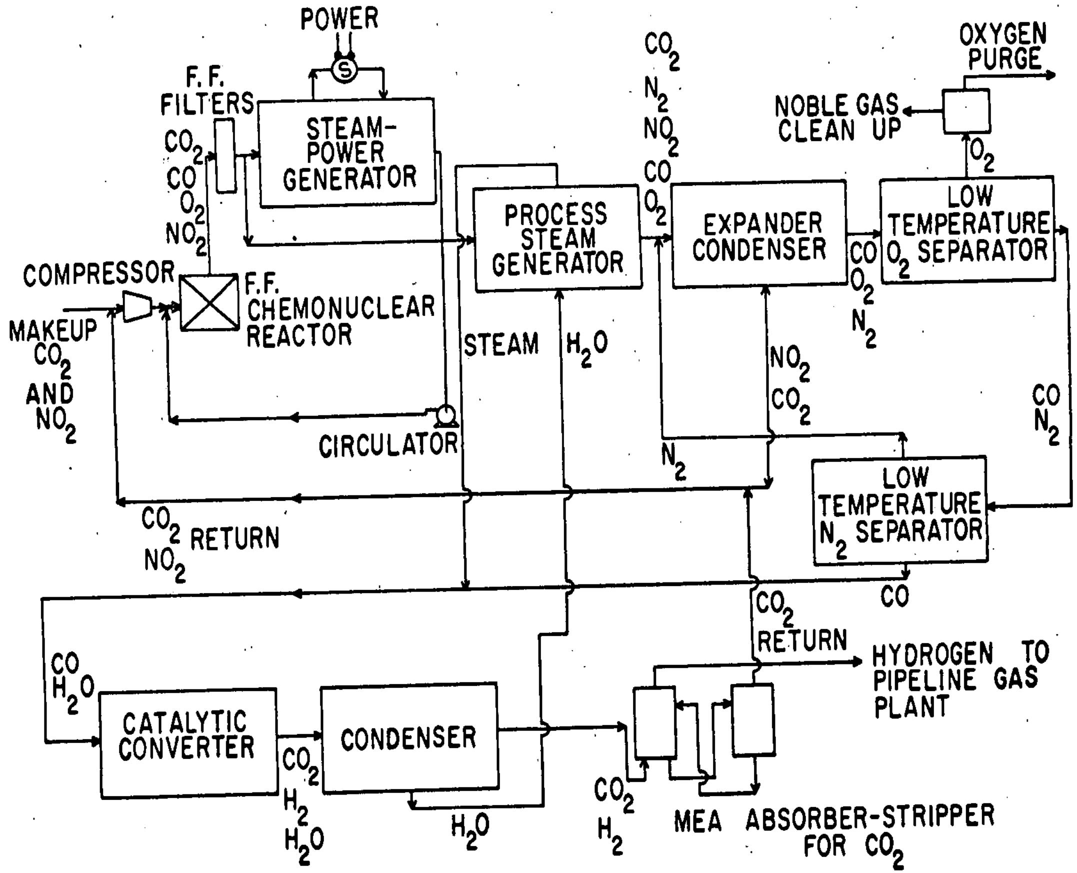
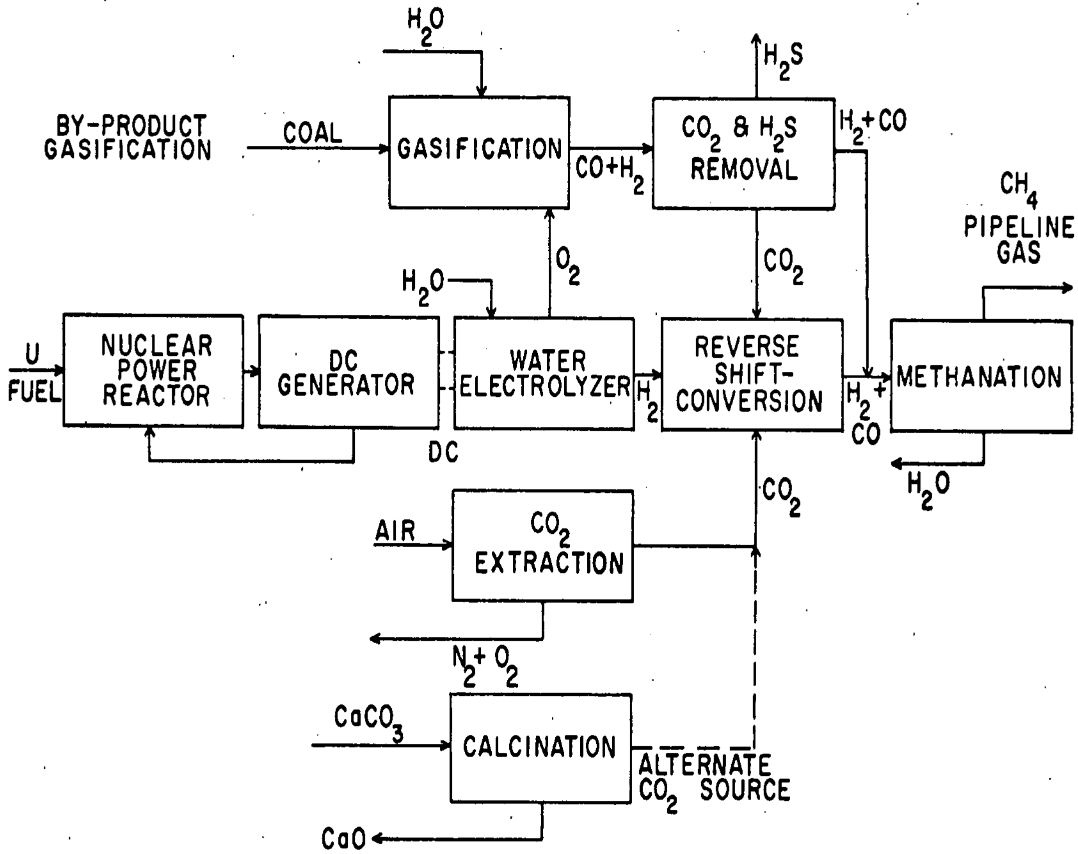



FISSION FRAGMENT CHEMONUCLEAR REACTOR FOR PRODUCTION OF CO AND $H_2$ FROM $CO_2$ AND FOR POWER PRODUCTION

Fig. 1




SYNTHESIS OF NON-FOSSIL PIPELINE GAS WITH NUCLEAR POWER AND BY-PRODUCT COAL GASIFICATION

Fig. 2