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Catalysis Today 35 (1997) 153–162

CATALYSIS TODAY

Catalytic technologies for energy production and recovery in the future

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Abstract

The paper gives an overview on modern trends in developing new catalytic technologies to use nuclear, nontraditional and renewable sources of energy, to produce mechanical or electrical energy from the energy of chemical energy carriers, as well as to recover middle or low-potential heat wastes and temperature gradients.

Keywords: Energy production; Energy recovery; Renewable energy sources

1. Introduction

The real far future of our civilization depends mostly on how we shall resolve the expected energy problems. Indeed, in case of absence some rigid limitations on the amount of energy in the mankind' disposal there will be no danger of a shortage of food, artificial motor fuel, artificial chemicals, etc. even for a 10 billion population of Earth [1].

There are two evident ways to overcome the future energy problems. First of all, one should increase the efficiency of usage of conventional energy carriers, that means simultaneously a necessity to diminish drastically the wastes or losses of energy. The second way is to enlarge utilization of nonexhaustible sources of energy which do still not create the basis of the nowadays energetics. A principal role in all these movements belongs to catalytic technologies.

Traditional way in application of catalytic technologies to energetics is their use for improvement of incineration of conventional or available fossil fuels in various large- or small-scale power plants. This allows to increase the heat-producing efficiency of these plants as well as to diminish pollution of the environment by toxic products of the fuel combustion. However, there are also some not so evident applications of catalytic technologies which may appear to be of a principal interest for the future.

In this paper, four lines of the modern trends in these fields will be concerned: (i) application of catalytic technologies to producing heat or high quality liquid fuels from renewable sources of carbon-containing raws (primarily, biomass); (ii) application of catalytic technologies to use nuclear and nontraditional sources of energy, (iii) producing the mechanical or electrical energy from the energy of chemical energy carri-

PII S0920-5861(96)00142-3

ers and (iv) recovery of middle- or low-potential heat wastes or utilization of some unexpected heat-energy sources (see also [2]).

2. Catalysis and catalytic technologies in utilization of biomass for needs of energetics. Production of heat or high quality liquid fuels from biomass and other renewable sources of carbon-containing raws

In future, renewable biomass of green plants and also municipal solid wastes (MSW) could appear to be the main carbon-containing raws for production of high quality liquid motor fuels (first of all, hydrocarbons) and valuable chemicals for chemical industry [1]. Note, that even now in Russia the annual production of industrial wood is only 2–3 times less, when comparing in calorific value, than that of fossil oil.

Possible implementation of catalysis and catalytic technologies for utilization of biomass could be numerous (see Fig. 1). Indeed, catalysis and catalytic technologies allow to create a basis for efficient utilization of biomass for solution of energy problems either via ecologically pure incineration and/or gasification of biomass (including wet biomass) or via its transformation into much more valuable energy carriers (e.g. liquid motor fuels).

Direct utilization of calorific ability of wet biomass for highly efficient production of technological heat can be achieved at the biomass incineration in fluidized bed of catalysts [2,3].

Catalytic incineration differs principally from incineration in the common sense, since the fuel is oxidized on the surface of granules of solid

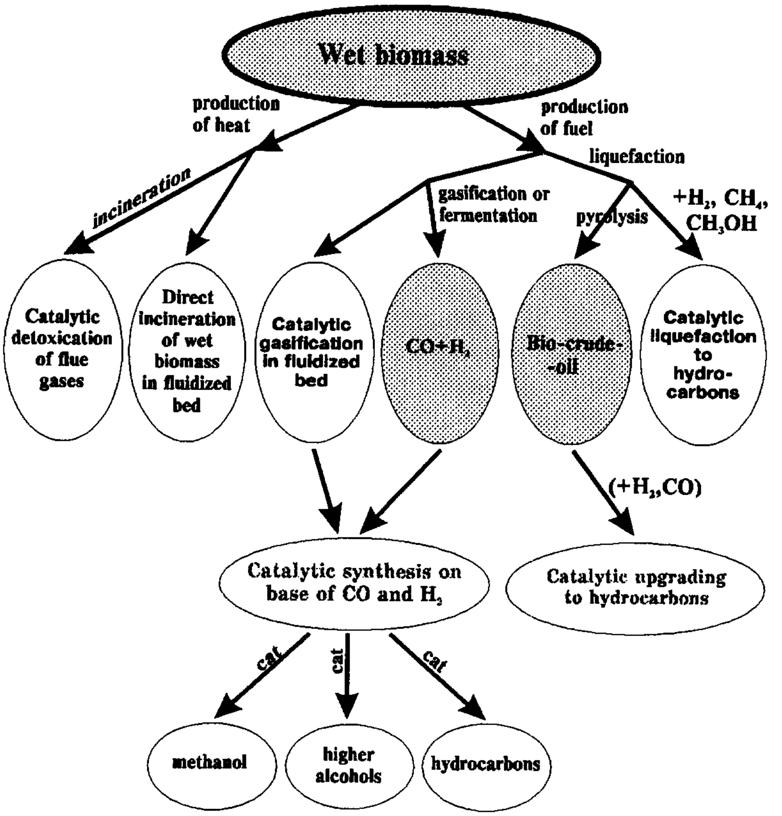


Fig. 1. The place of catalytic technologies in biomass utilization for needs of energetics.

catalysts at low enough temperature and without formation a flame. The catalyst' action in the process of complete oxidation (or "heterogeneous combustion") of air-fuel mixtures for many types of catalysts is based on interaction of fuel components with the "surface" oxygen of the catalyst with the successive regeneration of the reduced surface by oxygen from the gas phase.

In comparison with other known methods of incineration these peculiarities of heterogeneous oxidation make possible to diminish substantially demands to thermal resistance of the reactor construction materials and their erosion at the device operation, to diminish the heat losses through the reactor' walls as well as to achieve high (up to $400+\ \mathrm{kW/m^3}$) power loading of the incinerators. Of top importance is that the significant lowering of the incineration temperature diminishes also the losses of heat with the flue gases and excludes occurrence of secondary chemical reactions with formation of toxic products like NO_x, etc. Simultaneously, a more complete oxidation of organic constituents results in a much more complete utilization of calorific value of the low-quality fuel substrate partly by prevention of CO formation.

The most optimal conditions for catalytic incineration of wet biomass can be achieved in fluidized bed of catalysts. In this case at a relatively low temperature (400–700°C) one can arrange an efficient mass exchange and interaction of the particles of solid organic substrates with air and the surface of the catalyst through the gas phase, while the intermediates volatilized at this interaction are oxidized at the surface of the catalyst. At such condition chemically bounded nitrogen from the organic substrate is oxidized mostly to nontoxic dinitrogen. The toxic sulfur compounds are not evolved into the gas phase as well due to the low temperature and remain bounded to mineral constituents of the raw.

The Boreskov Institute of Catalysis has developed and tested bench and semi-industrial pilot plants based on these principles and feeded with highly wet sludges from the waste waters cleaning facilities as well as with wastes of the pulp and paper industry. A feasibility to use the same technology for ecologically pure gasification of biomass as well as for its drying is shown too.

Elaboration of efficient technologies for production of hydrocarbons from biomass and MSW are still under way. However, it is clearly evident, that the role of catalytic technologies here will be predominant, especially at the level of conditioning the products of primary conversion of biomass (see, e.g., [4]).

Of importance for catalytic chemistry is that transformation of biomass or the products of its primary conversion (e.g., bio-crude-oil, which is the very specific acidic liquid produced by rapid non-catalytic pyrolysis of biomass) into high-quality hydrocarbons or other kind of liquid motor fuels necessitates development of principally new catalytic processes of *deoxygenation* of some oxygen-rich compounds which are present in excess in biomass or bio-crude-oil.

As example of recent studies provided in the Boreskov Institute of Catalysis, one should mention development of several kinds of new processes and catalysts for deoxygenation of some main constituents of the bio-crude-oil [5]. Under development are here three ways of such deoxygenative upgrading the bio-crude-oil:

(1) Deoxygenation of some oxygen-containing bio-oil components with use of CO as deoxygenator via

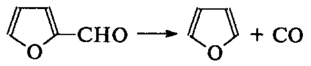
$$\mathrm{ROH} \xrightarrow{\mathrm{CO}} \mathrm{ROOH} \xrightarrow{-\mathrm{CO_2}} \mathrm{RH}$$

For example, bimetallic alloy RhCu on carbon is among the most efficient catalysts for carbonylation of phenol at 120–150°C and elevated CO pressure, while finely dispersed particles of PtPd or RuPd alloys behave as good catalysts for decarboxylation of benzoic acid to benzene at 220–260°C.

(2) Decarbonylation of aldehydes:

$$\mathrm{RCHO} \xrightarrow{-\mathrm{CO}} \mathrm{RH}$$

Mixed PbCs/sibunit catalyst has appeared to be efficient at 250°C for providing reaction



The catalysts were tested for treating not only model oxygenates, but also some prototypes of bio-crude-oil (e.g. rosin) as well as genuine bio-crude-oil. It has appeared unexpectedly that even bare carbon without metal promoters can be active in decarbonylation–decarbonylation reaction, that indeed is of extremely interest for developing commercial technologies for such treatment of biomass.

(3) Hydrogenolysis of bio-crude-oil at 20–100 atm of H_2 and 200–350°C on supported oxide or sulfide forms of NiMo or CoMo. A new type of molybdenum-based catalysts prepared from metallocomplex precursors have exhibited pronounced properties in deoxygenative hydrogenolysis of furane-like compounds, which seem to be the main reason for nonstability of the bio-crude-oil. Artificial porous carbon "sibunit" has been chosen as the most promising support. This support is free of main disadvantages of aluminas or zeolites which are dissolved or distracted by acidic bio-crude-oil.

It is of interest that properties of the latter hydrogenolysis catalysts under test appeared to be dependent on nuclearity of the Mo ion containing active centra, the centra with two or three Mo ions being totally inactive in polymerization of furane-based compounds. The last observation could be of top importance for processing the easy-polymerized bio-crude-oil.

Note also, that of an importance for future could appear still nonexisting technologies of direct deoxygenation (enrichment with hydrogen) of biomass by its catalytic coprocessing with natural gas or polymeric wastes. The latters are considered to be a large-scale high-quality renewable raw for the future as well.

3. Catalytic technologies in nuclear and non-traditional energetics

Two non-exhaustible sources of primary energy are of the most interest for far future. These are nuclear energy released by either fission or fusion nuclear processes and solar light. The direct use of both these primary energies is impossible, since they have to be converted into a suitable form. Catalytic processes are capable of converting into energy of chemical bonds any of the above mentioned kinds of energy and to store it in the form of chemical fuels.

The simplest idea for conversion and storage of such energy is utilization of highly reversible

Table 1

Reversible catalytic reactions proposed for thermocatalytic conversion of energy at nuclear and solar plants and in chemical heat pumps, and their thermodynamic parameters

N	Reactions [a]	ΔG°_{298} (kcal/mol)	ΔH°_{298} (kcal/mol)	ΔS°_{298} (cal/mol K)	T^{*} [b] (K)
1	$SO_3(g) \rightarrow SO_2(g) + 1/2\ O_2$	16.7	23.5	22.5	1030
2	$C(s) + H_2O(l) \rightarrow H_2 + CO$	23.9	41.9	60.4	980
3	$C(s) + CO_2 \rightarrow 2\ CO$	28.6	41.3	42.2	980
4	$CH_4 + H_2O(l) \rightarrow 3\ H_2 + CO$	36.0	59.8	79.7	960
5	$CH_4 + CO_2 \rightarrow 2\ H_2 + 2\ CO$	40.8	59.1	61.5	960
6	$C_6H_{12}(g) \rightarrow C_6H_6(g) + 3\ H_2$	23.4	49.3	86.6	570
7	$C_6H_{11}CH_3(g) \rightarrow C_6H_5CH_3(g) + 3\ H_2$	22.7	48.9	88.0	560
8	$NH_3(g) \rightarrow 1/2\ N_2 + 3/2\ H_2$	4.0	11.0	23.7	470
9	$CH_3OH(g) \rightarrow 2\ H_2 + CO$	6.0	21.7	52.3	415
10	$CH_3OH(l) + H_2O(l) \rightarrow 3\ H_2 + CO_2$	2.1	31.2	97.7	320
11	$CH_3CHOHCH_3(g) \rightarrow CH_3COCH_3(g) + H_2$	5.6	14.1	28.5	495

[a] (g) – gaseous; (l) – liquid; (s) – solid.

[b] T^{*} is the temperature at which $\Delta G^{\circ} = 0$

processes capable to shift their equilibrium when the temperature of the system is changed (see Table 1).

As to the nuclear fission energetics, the so-called EVA-ADAM catalytic technology is well known for indirect accumulation of released nuclear energy in the form of syngas, its storing and transportation on large distances (see Fig. 2a). Recently, a new much more efficient ICAR (Immediate Catalytic Accumulation of ionized Radiation energy) process was suggested for direct nuclear-to-chemical energy conversion (see Fig. 2b and [6]). The peculiarity of ICAR technology consists of placing the energy-converting catalysts immediately into the active energy-releasing zone of a nuclear reactor or even usage of special multifunctional physicochemical structures serving simultaneously as a nuclear fuel and a catalyst for the energy-storing chemical reaction (e.g. porous uranium oxide impregnated with catalytically active metal Ni or Ru [7]).

ICAR process has exhibited a high efficiency of nuclear energy conversion combined with ability to maintain the useful specific power loading of the energy conversion up to 100–200 kW/dm^3. These last figures correspond to those for energy release in the modern fission nuclear power plants. ICAR technology can also be widely used in the fusion thermonuclear energetics, since it seems to be the only technology which will allow to utilize the enormous fluxes of ionizing radiation released by the future thermonuclear fusion reactors.

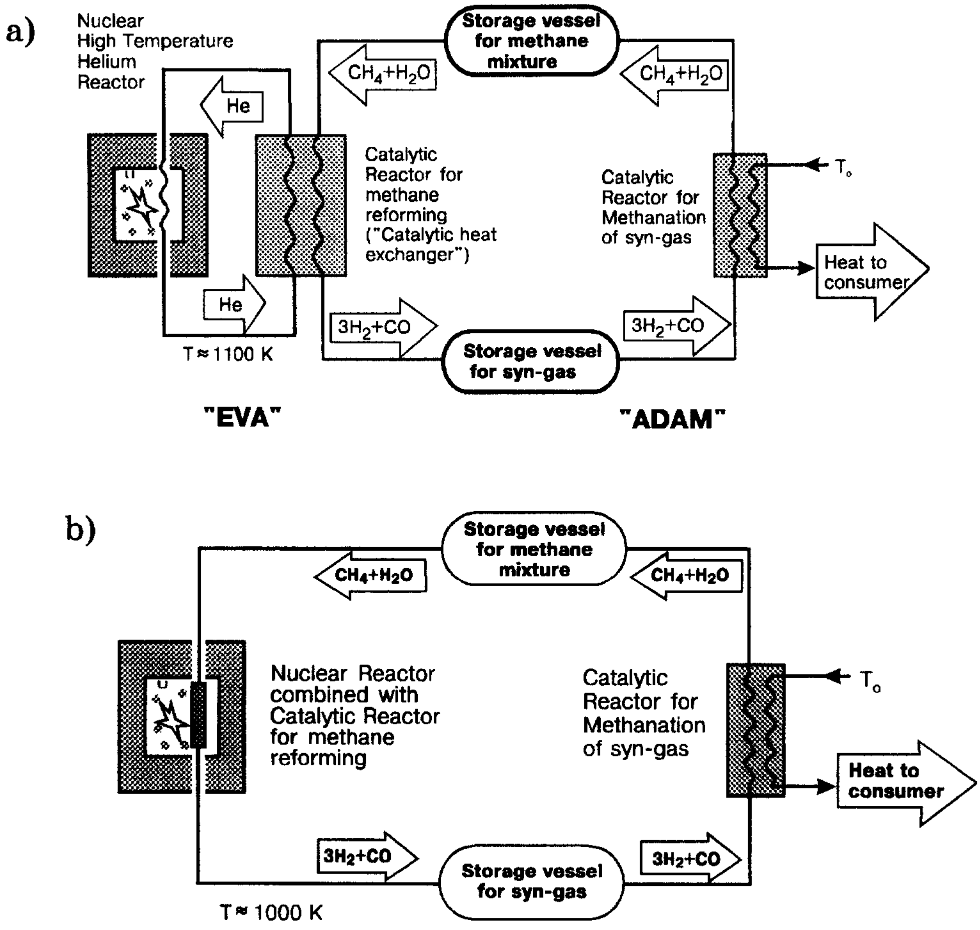


Fig. 2. Principal schemes of the EVA-ADAM (a) and ICAR (b) cycles of thermocatalytic conversion of nuclear energy. Reversible reaction of the steam reforming of methane is used as the energy converting process in the both cases.

Table 2
Thermodynamic parameters of reactions between water and atmospheric gases as reactants which are promising for photocatalytic conversion of solar energy

N	Reactions	$\Delta G^{\circ a}_{298}$ (kcal/mol)	$\Delta H^{\circ a}_{298}$	λ_0 ^{b} (nm)
1	$H_2O \rightarrow H_2 + 1/2\,O_2$	56.7	68.3	1008
2	$H_2O + CO_2 \rightarrow HCOOH + 1/2\,O_2$	68.4	64.5	836
3	$H_2O + CO_2 \rightarrow CH_4O + O_2$	124.8	134.6	916
4	$H_2O + CO_2 \rightarrow H_2 + CO + O_2$	118.2	135.9	969
5	$2\,H_2 + CO_2 \rightarrow CH_3OH + 1/2\,O_2$	167.9	173.6	1025
6	$2\,H_2O + CO_2 \rightarrow CH_4 + 2\,O_2$	195.5	212.8	1176
7	$3\,H_2O + CO_2 \rightarrow C_2H_5OH + 3\,O_2$	318.3	336.8	1077
8	$H_2O + CO_2 \rightarrow 1/6\,C_6H_{12}O_6 + O_2$	114.7	111.6	997
9	$3/2\,H_2O + 1/2\,N_2 \rightarrow NH_3 + 3/4\,O_2$	81.1	91.4	1059
10	$2\,H_2O + N_2 \rightarrow N_2H_4 + O_2$	181.3	148.7	629

[a] ΔH° and ΔG° values are given for liquid H_2O, HCOOH, CH_3OH, and N_2H_4 and solid $C_6H_{12}O_6$; other compounds are taken to be gaseous.

[b] λ_0 is the threshold wavelength for a photochemical process causing the reaction.

In the last two decades serious efforts were made to develop catalytic processes for solar energy conversion. One path in this research deals with *quantum photocatalytic* processes which provide production of high quality fuels such as hydrogen (see Table 2) upon any type of solar irradiation, including highly scattered. Much more advanced are developments for *nonquantum thermocatalytic* processes of conversion of concentrated solar energy (see Fig. 3).

Already in the early 80's the prototypes of energy converting installations of a reasonable useful power (more than 2 kW) and of a very high (more than 40%) efficiency of solar-to-chemical energy conversion were tested [8]. Under way is further development of design and other improvements of such solar energy converting systems [9,10].

An interesting application of catalytic technologies to the thermochemical methods of nuclear or solar energy conversion could be cre-

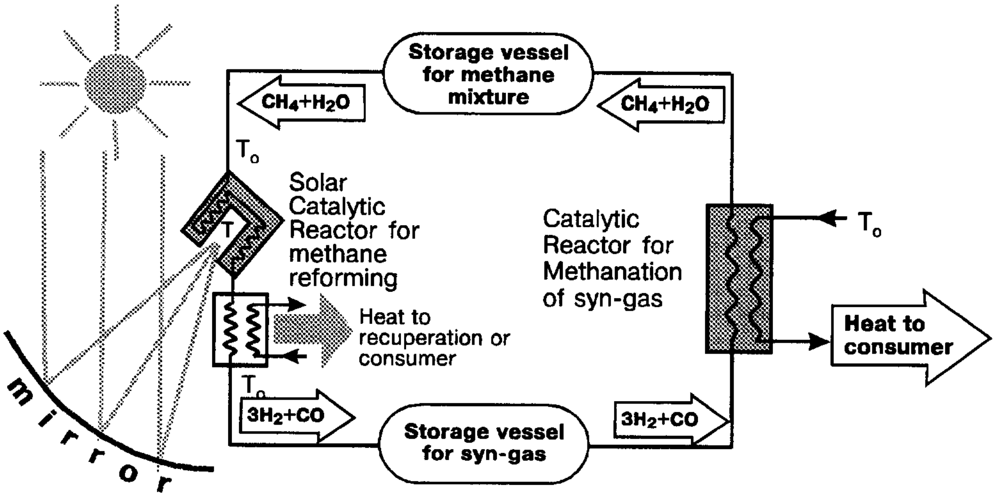


Fig. 3. A principal scheme of thermocatalytic conversion of solar energy based on the idea of the EVA-ADAM cycle.

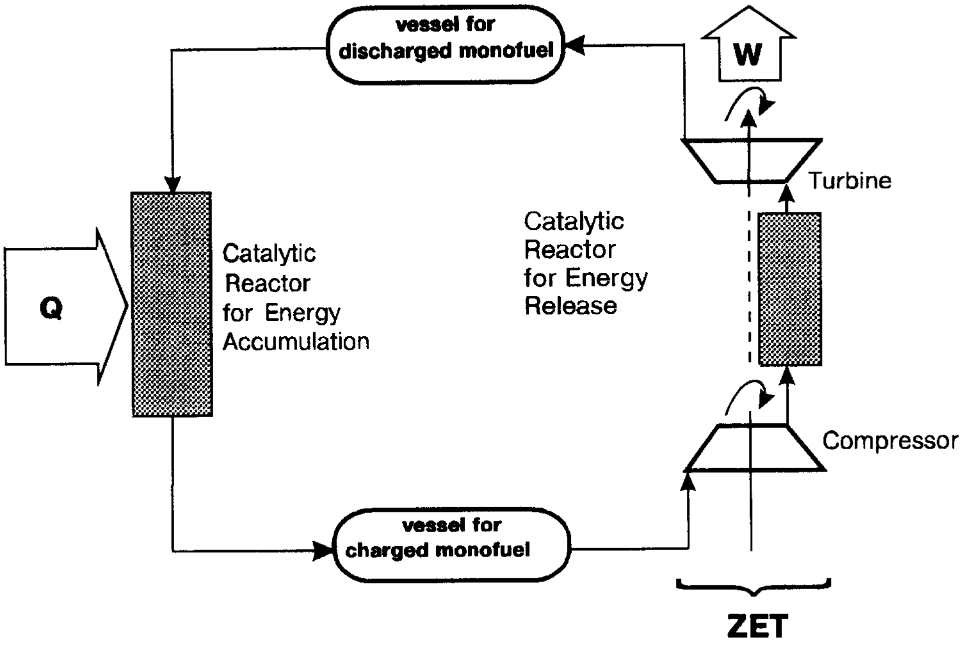


Fig. 4. A scheme of direct chemical-to-mechanical energy conversion in the "Zero Emission Turbine" (ZET) with use of reversible fuel mixtures. *Q* stands for a primary (heat) energy flux consumed for its accumulation and further release as work *W* (or electricity as well).

ation of "Zero Emission Turbines" (ZET) which utilize chemical reversible "monofuels" (i.e. those which do not need a separation or mixing of their components during production or utilization of the fuel) and allow to combine total ecological safety of the power plants with a highly efficient conversion of the energy of the chemical fuel into mechanical energy without intermediate heat exchangers (see Fig. 4 and [11]). For example, in case of utilization of the mentioned reversible syn-gas methanation – methane reforming reactions, the efficiency of chemical-to-mechanical (electrical) energy conversion in ZET can achieve the value of 50% at

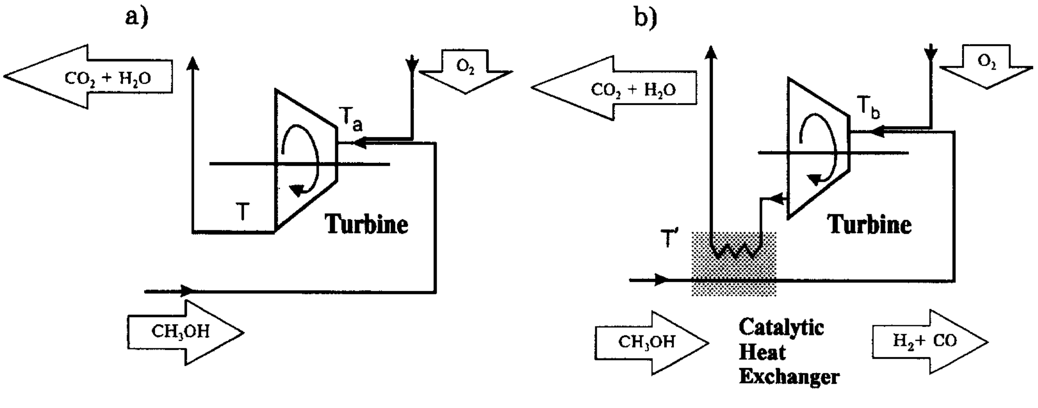


Fig. 5. Schemes of a gas-turbine operation in a conventional mode (a) and in a mode with catalytic heat recuperation (b). Calorific value of the fuel (methanol) is increased by its pretreatment with hot exhaust gases of the turbine, thus increasing the total energetic efficiency of chemical-to-mechanical energy conversion.

a reasonable (no greater than 20-fold) compression of syn-gas at the ZET inlet.

4. Catalytic technologies in increasing the efficiency of mechanical and electrical energy production

During the last decade, a great interest is paid to application of catalysis for improving the efficiency of mechanical engines. One approach is based on improvement of fuel combustion in gas turbines or in piston engines. The second one is based on nontraditional ideas of the so-called ''*catalytic heat recuperation*'' providing a sufficient (up to 10–15%) increase in the efficiency of a thermal engine (even over the value given by the conventional Carnot cycle, see Fig. 5) through using the heat of exhausted gases for catalytic pretreatment of chemical fuels to enrich their calorific value.

A non-expected implementation of this idea is usage of ''catalytic heat recuperation'' for cooling the overheated units of hypersonics with simultaneous increase of the efficiency of its propulsion ability due to enrichment of fuel with energy (see [12] and Fig. 6).

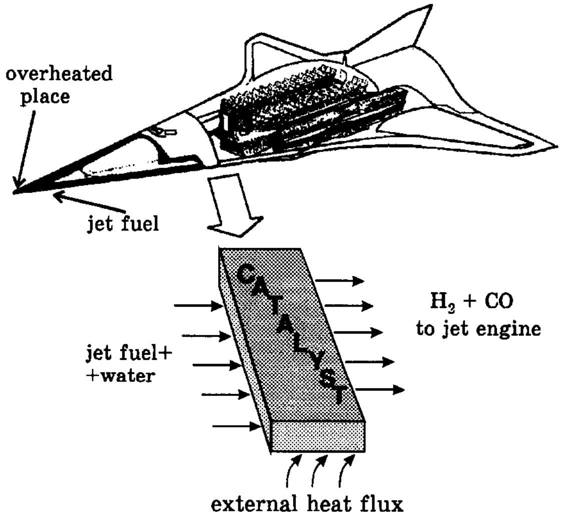


Fig. 6. Thermocatalytic pretreatment of jet fuel conjugated with cooling of the aircraft in the Russian hypersonic ($v = 10000$ km/h) ''Neva'' for the XXI century.

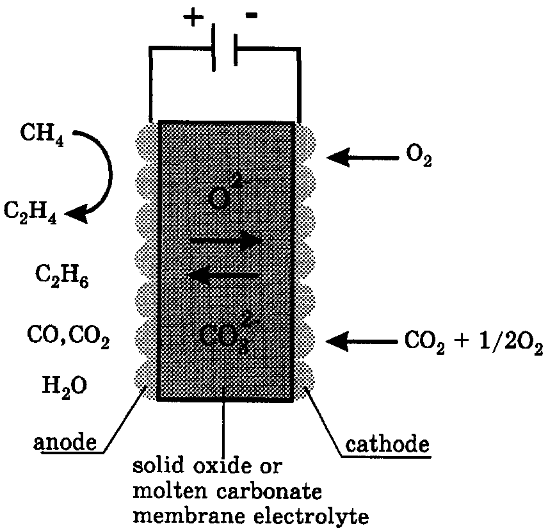


Fig. 7. A principal scheme of cogeneration of electricity and valuable chemicals (C_2 hydrocarbons) in a high temperature fuel cell utilizing methane as the fuel.

The principal improvements of the electricity production are obtained in the field of fuel cells. Most promising are, certainly, high-temperature ''molten carbonate'' or ''solid oxide'' fuel cells which allow to use either conventional fuels, such as natural gas, gasoline, etc., or gasified MSW, biomass, etc. An ''*external*'' or ''*internal catalytic reforming*'' of these fuels is an inevitable element of all such fuel cells.

Of a top interest are recent findings in the field of high-temperature fuel cells, which revealed their ability to operate in a mode of co-generation of both electricity and some valuable chemicals [2]. One of the most promising applications is production of C_2 hydrocarbons (ethane, ethylene) or syn-gas by the ''high temperature'' fuel cells fed with natural gas (see Fig. 7).

Recently, the first positive results were obtained in direction of cogeneration of electricity and oxygenates at mild (near room temperature and pressure) oxidation of light paraffins (ethane) by air oxygen in a ''cathodic'' mode of the oxidation [13].

5. Catalytic technologies for recovery or utilization of middle- and low-potential heat

Catalytic technologies can be efficiently used for utilization of middle- and low-potential heat (200–500°C and even lower than 200°C), yielding by various industrial heat wastes, geothermal water, etc. The main developments in this field are focused on using the so called *"chemical heat pumps"* based on middle- and low-temperature reversible catalytic reactions of dehydrogenation/hydrogenation (see Table 1 and Fig. 8) or dehydration/hydration types [2].

Chemical heat pumps reveal some potential advantages as compared to the conventional heat pumps which are based on chemically inactive "working body". The main advantages are a possibility to find suitable substrates for desirable levels of temperature and to store the converted heat for any time in the form of chemical energy.

An ability to accumulate and store the low- and middle-potential heat is given as well by new materials with large absorption capacity. The most attractive materials are zeolites and the so-called chemisorbents. When using very simple substrates as adsorbates (say, water, carbon dioxide, oxygen, etc.), these materials are able to accumulate up to 2000 kJ/dm^3 of heat even in the ambient temperature interval [14]. This provides a new powerful tool for recovery heat wastes and for efficient utilization of the natural either day-to-night or season temperature gradients as well as for design of nontraditional freon-less air-conditioning systems, etc. Note, that in countries with the rigid continental climate, day-to-night and season temperature gradients seem to create a nonexpected energy source with anormous potential.

An important contribution to utilization of middle-potential heat could be made also by new catalytic technologies of cleaning geothermal steam from hydrogen sulfide by its direct oxidation to sulfur without loosing the energetic potential of the steam.

6. Conclusion

The above data on the modern trends in developing the catalytic technologies for the

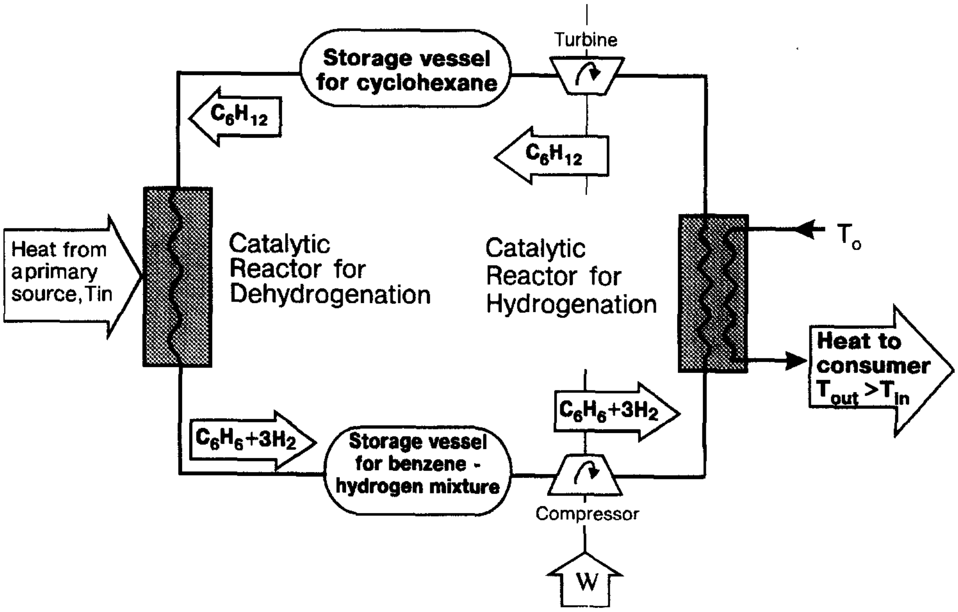


Fig. 8. An example of a principal scheme of a chemical heat pump on the base of reversible catalytic process of the cyclohexane dehydrogenation/benzene hydrogenation.

energy industry evidence for their large potentialities. No doubt, that some of such technologies will find a wide application already in the near future. An accelerated development of these technologies seems to be one of the most important task for both chemical and power engineering as well as for chemical science.

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