ETHANOL AND OTHER OXYGENATEDS FROM LOW GRADE CARBONACEOUS RESOURCES

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Abstract

Anhydrous ethanol and other oxygenates of C2 up can be produced quite competitively from low grade carbonaceous resources in high yield via gasification, methanol synthesis, carbonylation of methanol and hydrogenation consecutively. Gas phase carbonylation of methanol to form methyl acetate is the key step for the whole process. Methyl acetate can be produced very selectively in one step gas phase reaction on a fixed bed column reactor with GHSV over 5,000. The consecutive hydrogenation of methyl or ethyl acetate produce anhydrous ethanol in high purity. It is also attempted to co-produce methanol and DME in IGCC, in which low grade carbonaceous resources are used as energy sources, and the surplus power and pre-power gas can be stored in liquid form of methanol and DME during base load time. Further integration of C2 up oxygenate production with IGCC can improve its economics. The attempt of above extensive technology integration can generate significant industrial profitability as well as reduce the environmental complication related with massive energy consumption.

Introduction

In this presentation, gas conversion will be focused as a mean of clean energy development. There have been many research efforts on higher alcohol synthesis from syn gas which is produced from low grade carbon sources. The major draw back from the results of the research efforts is selectivity of the products. Two approaches will be presented for the purpose: one is ethanol synthesis and another one is dimethyl ether synthesis from syn gas. Increasing attention has been paid to ethanol as a potential oxygen carrier and octane booster in gasoline. However, the ethanol price is the major obstacle to be used for such purpose. Currently, ethanol is produced by fermentation or ethylene hydration. Therefore, ethanol from such process is too expensive to be used in gasoline without government subsidies such as tax benefit. Indeed, this problem is the hottest issue among the end users and the manufacturers particularly grain producers. A number of routes from C1 to ethanol have been proposed by the several major research groups from industries during last decade or so in the light of the importance as oxygen carrier in gasoline. Three meaningful routes of these alternative approaches will be discussed briefly to review the back ground in this field. Direct synthesis of ethanol from syn gas has been studied in vapor phase reaction over supported transition metal catalyst under severe reaction conditions(1-4). Only alcohol mixture which contains mostly methanol and 40 - 50% of ethanol at most can be obtained even under high reaction pressure of 1,800 - 2,000 psi. Second one is methanol homologation to ethanol using cobalt-ruthenium halide under even higher reaction pressure of 4,000 - 5,000 psi(5-6). The selectivity to ethanol is 60 - 80% which is higher than the direct synthesis. However, the mixture product includes other alcohols and their acetate ester. In any cases, the reaction conditions are severe and the purity of the ethanol is rather low. The last one is hydrogenolysis of methyl or ethyl acetate which is produced from esterification of acetic acid with methanol or ethanol(7-9). Since expensive acetic acid is used as starting material and esterification of the acetic acid with methanol removing equivalent amount of water is involved, the manufacturing cost is very high. To improve the above processes, an alternative route is presented to produce ethanol from cheap low grade carbon resources such as coal, natural gas and even bio mass. The first step to utilize such low grade carbonaceous resources is gasification to produce syn gas. The commercially amenable chemical process from syn gas is methanol synthesis at this time and the process is one of the best established chemical technology. Therefore, methanol is taken as common starting material from a well established technology. There have been many reports on C2 chemical synthesis from C1. But, there are very few reactions which can convert C1 to C2 selectively in reasonably good yields. Methanol carbonylation is the only commercial process to make C2 from C1 selectively in high yield. However, the current commercial process of methanol carbonylation is conducted in liquid phase which entails severe corrosion problem and large quantity acetic acid recycle as solvent. In this work, the gas phase methanol carbonylation has been successfully conducted to make acetic acid as well as methyl acetate selectively with high productivity. Particularly, methyl acetate can be produced selectively in one step in the gas phase carbonylation and make it possible to produce anhydrous ethanol and other oxygenate chemicals quite competitively to be used as commodity chemicals. Further more, DME was reported as an excellent substitute for diesel fuel(11). The performance test showed excellent results with respect to emissions, efficiency and noise. Large scale DME production instead of methanol being integrated with IGCC will be discussed here to enhance economic of DME production as well as IGCC.

Ethanol Production

To improve the current ethanol synthesis, methanol carbonylation is employed as a key step to make C2 chemicals from C1 most selectively. The C2 chemical intermediate in this process is methyl acetate which is hydrogenated to ethanol subsequently. The schematic diagram of the process from methanol to ethanol is shown in the Fig. 1. In the process, 2 moles of methanol are taken as feed stock to form 1 mole of methyl formate and 2 moles of hydrogen. The methyl formate formed by dehydrogenation of methanol can be decomposed to one mole of methanol and CO which are introduced consecutively into methanol carbonylation reactor in gas phase to form methyl acetate. The methyl acetate formed is reduced by the hydrogen, which is produced from the methanol dehydrogenation reaction, to produce one mole of ethanol and methanol correspondingly. The methanol is recycled to the carbonylation reactor. As the result, one mole of ethanol is produced from 2 mole of methanol.

-Methanol carbonylation in gas phase

The methanol carbonylation has been done commercially in liquid phase to produce acetic acid in presence of rhodium catalyst and iodide promoter such as methyl iodide. It is highly desirable to do the carbonylation in gas phase since the liquid phase reaction accompanies serious problems such as corrosion and side reactions due to extensive residence time under severe reaction conditions. There have been several reports on gas phase carbonylation of methanol. However, they have not been successful with catalyst life time in the gas phase carbonylation due to deactivation and fast elusion of the active species from the support. KIST has developed a noble method to prevent the catalyst elusion from the support and maintain the longevity of the catalyst for long time during the gas phase carbonylation.

$$CH_3OH + CO \longrightarrow CH_3COOCH_3 + CH_3COOH + H_2O$$

The reaction has been conducted in a fixed bed column with 100% conversion and high selectivity toward acetic acid and methyl acetate in the ratio of from 15/85 to 85/15 under relatively mild conditions. The product ratio is freely controllable within the range shown above by simple change of the reaction conditions. This catalytic system showed high activity and low corrosion problem. It enables that. the gas phase carbonylation is very useful for practical application to produce C2 chemicals such as acetic acid and methyl acetate from C1. In this presentation, methyl acetate is the main concern and will be discussed extensively. As the result, C2 compounds can be prepared successfully starting from CO and methanol which can be achieved readily from low grade carbonaceous resources such as coal and natural gas employing well established commercial technology.

-Ethanol from methyl acetate

Once the methyl acetate is obtained with a competitive cost, the ester can be readily hydrogenolized to produce ethanol using copper based catalyst.

$$CH_3COOCH_3 + H_2 \xrightarrow[\text{Cu-ZnO}]{220^\circ C,\ 500psi} CH_3CH_2OH + CH_3OH$$

As indicated above, hydrogenolysis of methyl or ethyl acetate to produce ethanol have been patented and reviewed extensively (7-9). However, the process has been left as uneconomic one to produce ethanol from rather expensive acetic acid until now. KIST has developed a one step noble process in a simple fixed bed column to produce methyl acetate with very competitive cost from methanol and carbon monoxide which can be readily obtained from low grade carbonaceous resources via well established gasification technologies. Hydrogenation of methylacetate was performed in gas phase to produce 1:1 mixture of ethanol and methanol in the presence of copper based catalysts. Commercially available catalysts showed good activities, but they need rather vigorous reaction conditions. The catalysts which have been developed at KIST were examined under the conditions of 220°C, 500psi, and H_2/CH_3COOCH_3=5/1(fig. 2). The selectivity was high and part of the ethanol formed reacted with methyl acetate to produce ethyl acetate as a major by-product under the reaction conditions with low conversion.

-Other C2 up oxygenate chemicals from methyl acetate
Methyl acetate is further carbonylated to produce acetic anhydride which is used in production of cellulose acetate from cellulose. Transesterification of methyl acetate with corresponding alcohols, which can be conducted rather simply in a reactive distillation column, can produce acid free alkyl acetates competitively without generating water which causes reversible reaction to give carboxylic acid in the product. The competitive production of methyl acetate can improve the economic of vinyl acetate process via methyl acetate carbonylation which has been studied extensively by many research groups. Some of the potentially important chemical reactions starting from methyl acetate are shown in the following chemical equations.

- $CH_3COOCH_3 + CO \longrightarrow CH_3COOCOCH_3$
- $CH_3COOCH_3 + ROH \longrightarrow CH_3COOR + CH_3OH$
- $CH_3COOCH_3 + CO/H_2 \longrightarrow CH_3COOCH{=}CH_2$
- $CH_3COOCH_3 \longrightarrow CH_3CH_2COOH$

The value added chemical production from methanol could improve the economics of IGCC through further integration with the processes involved.

DME Production for Further Integration in IGCC

Due to fast depletion of high grade energy source, more and more attention has been paid to first low grade energy source such as coal, natural gas and other low grade carbonaceous resources. Power generation from the first low grade energy source is very popular in the light of low cost. However, this kind of power generation entails environmental implication and intrinsic problem of power peak control due to power demand fluctuation. More specifically, the usage of low grade carbonaceous resources for power generation requires gasification first and the gas product, which is known as syn gas(CO/H_2), must be cleaned from SOx and NOx. The syn gas prepared is ready to be burned in the gas turbine to produce electricity and the heat in the gas is used to generate steam which is used in the steam turbine consecutively to generate electricity further. As indicated above, the power generation burning low grade carbonaceous resources particularly coal has an intrinsic problem of peak management due to the power demand fluctuation. It is attempted to alleviate the inefficiency of the power generation due to the power demand fluctuation combining with methanol plant, where the surplus power and pre-power-gas can be stored into a storable and transportable liquid of methanol(fig. 3). If 10% of the average energy is transformed into a liquid chemical such as methanol at a power plant with a capacity of 500Mw burning 3230,000 ton/year, 109,000 ton/year of methanol can be produced. This way, the surplus energy can be stored in an ideal chemical form of methanol which can be used readily as desired. It is widely recognized that the methanol is the building block of C1 to open a new era of chemical industry for the future starting from low grade carbonaceous resources including even renewable biomasses. The methanol from such an integrated technology combining energy and chemical mass commutation is significantly cheaper than from regular methanol plant. The integration of the related technologies, which is known as IGCC(Integrated Gasification Combined Cycle electric power generation), has been extensively studied by many expert groups in this field to find sound economic feasibility of the approach(10). However, commercialization of the IGCC to generate power and chemical mass has not been practiced yet due to massive large scale integration of broad technologies. When the IGCC is commercialized, there will be a major change in chemical technologies starting from methanol. Since the economic of the ethanol production depends heavily on the cost of methanol and CO, methanol and CO from IGCC will improve the cost of ethanol production great deal(fig. 4). In such case, ethylene from ethanol dehydration would be quite popular with a small scale merit. Further more, CO2, which is considered to be the major cause of the green house effect, can be recycled as energy storage media in the mimesis of natural photo synthesis. It is obvious that hydrogen, which can be produced from abundant water on the earth utilizing solar energy or waste energy, will be the future energy source. The hydrogen produced will be stored in CO2 via appropriate catalysis to form methanol which is feasible with currently available technologies. Methanol synthesis from carbon dioxide has the intrinsic problem of water formation which is the cause of unfavorable equilibrium limit. However, we have managed to over come the limitation through multi stage synthesis loop to meet the optimum CO2/CO/H2 ratio for the feed gas. Further more, any organic refuses which can be gasified could also be put into the cycle through gasification to alleviate environmental implication.

It has been reported that DME is a clean fuel which shows excellent engine performance replacing diesel fuel which is known as the major urban pollution source(11). If DME could be used as clean urban fuel replacing diesel, large volume of DME should be produced. The large scale DME production from pre-power syn gas produced in a power plant as a mean of power peak control during the base load time could supply reasonably cheap clean fuel for the urban transportation eliminating the heavy initial investment for syn gas generation. The investment breakdown of a methanol plant shows that more than 50% of the initial investment is for syn gas preparation. DME synthesis from pre-power syn gas of IGCC could be advantageous to methanol synthesis which has unfavorable thermodynamic limitation. In the reaction the formation of DME is favored to that of methanol under the given reaction conditions. It has been found that one through conversion of the syngas in the lab. scale is more than 80% under 1,500 psi at 240°C with the space velocity of 10,000/hr. The power peak control problem will be alleviated by further integration with relevant chemical technology such as DME production from the pre-power gas. Since coal will be major organic energy sources replacing oil, clean coal technology come to our attention increasingly. Therefore, IGCC will be the common power generation technology in the near future, and DME will even be produced from any low grade carbon sources such as biomass and organic refuses from our daily life. It would be also highly desirable to convert these organic refuses to syn gas and DME clean fuel for the urban transportation. Further more, DME could be produced instead of methanol as a mean of hydrogen storage in CO2 as described above.

Conclusion

It can be concluded that the integration of the technologies in power generation and chemical mass production is highly desirable to develop alternative clean energy sources and other chemical raw materials from low grade carbon sources such as coal and natural gas replacing oil. Further more, it is essential to develop clean technology to avide with the nature on this planet. Ethanol and DME are know as good oxygenated chemical compounds to be used as clean fuel or additive. The methanol carbonylation in gas phase can provide an excellent process to produce anhydrous ethanol. The integration of these kind of technologies can alleviate the high cost of clean technology. Our effort in the further integration of the related technologies will realize the dream of clean environment and promote the development of alternative energy and chemical sources in near future.

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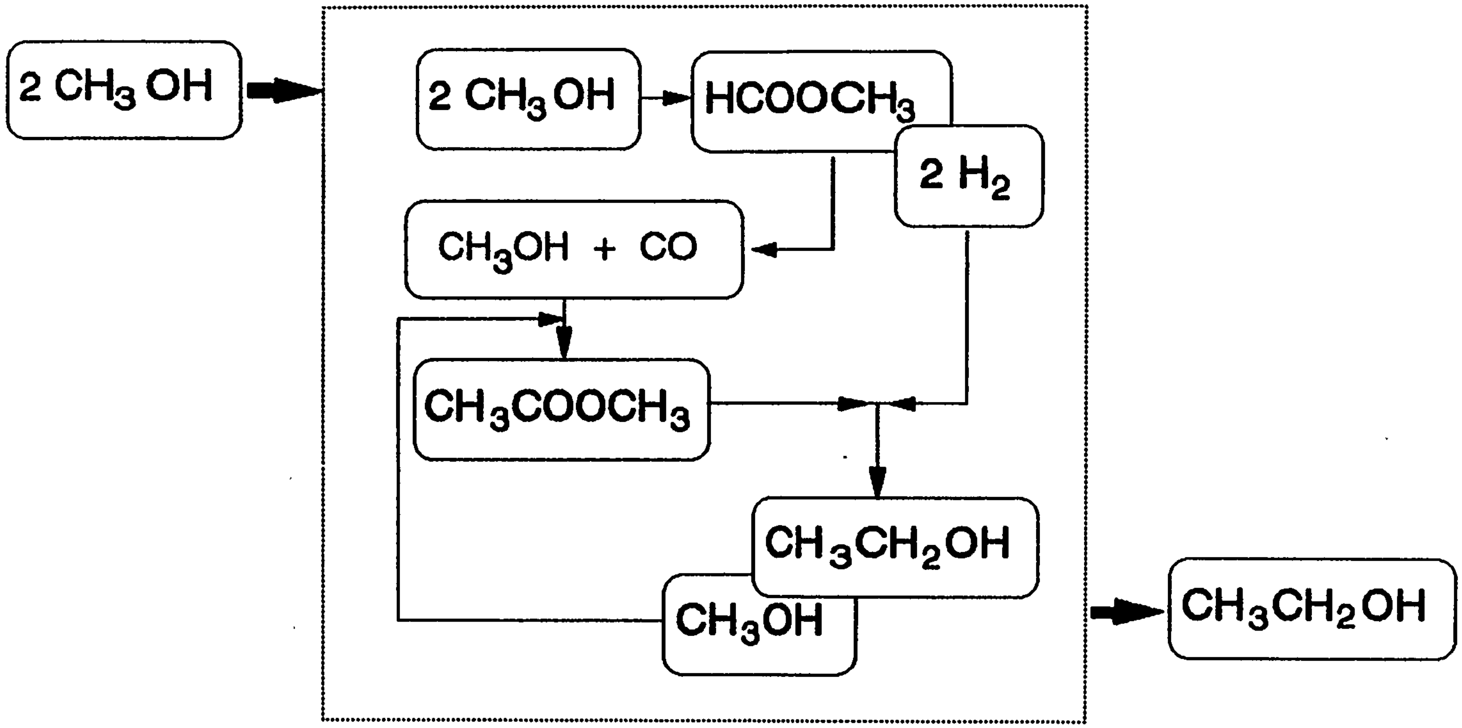

Figure 1. The schematic diagram of the process from methanol to ethanol.

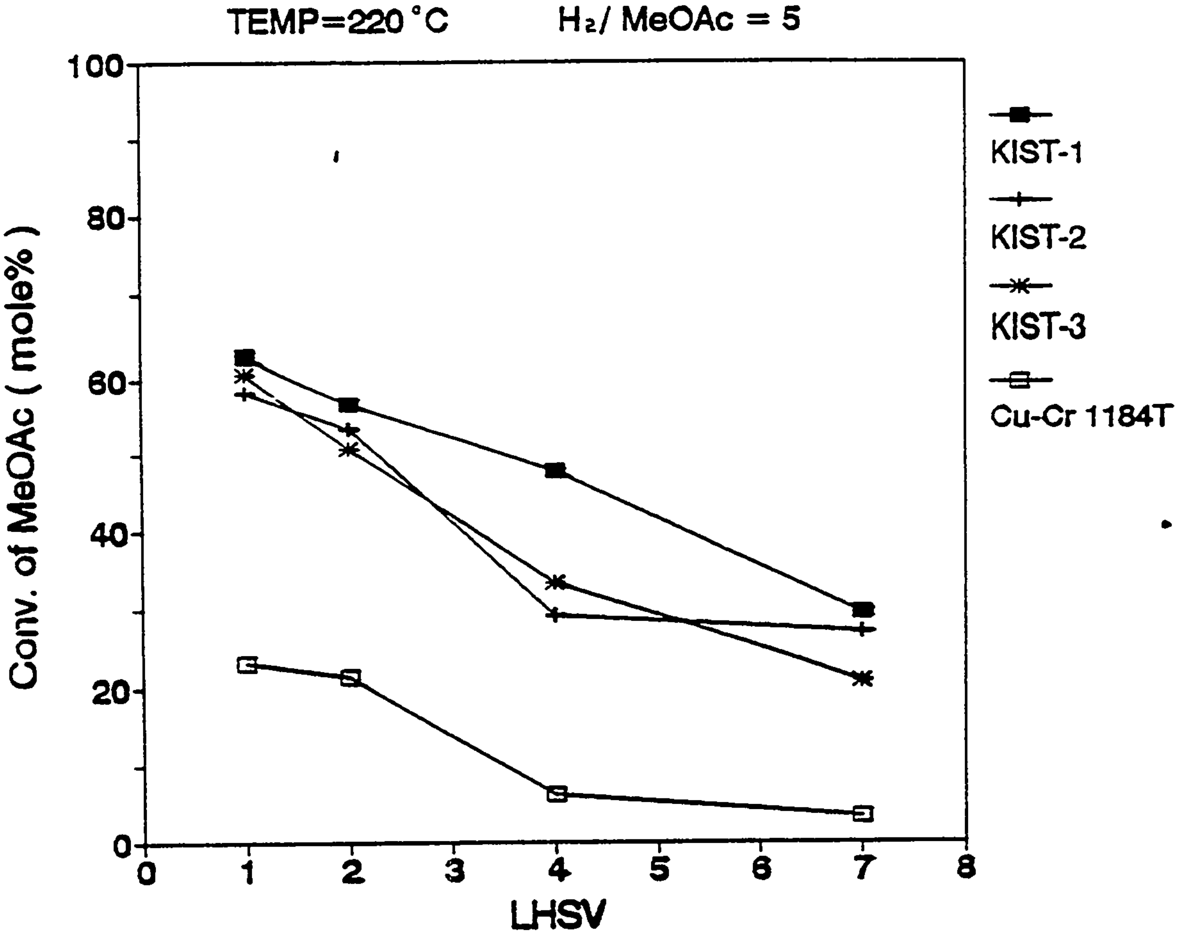

Figure 2. Hydrogenolysis of methyl acetate on various catalysts.

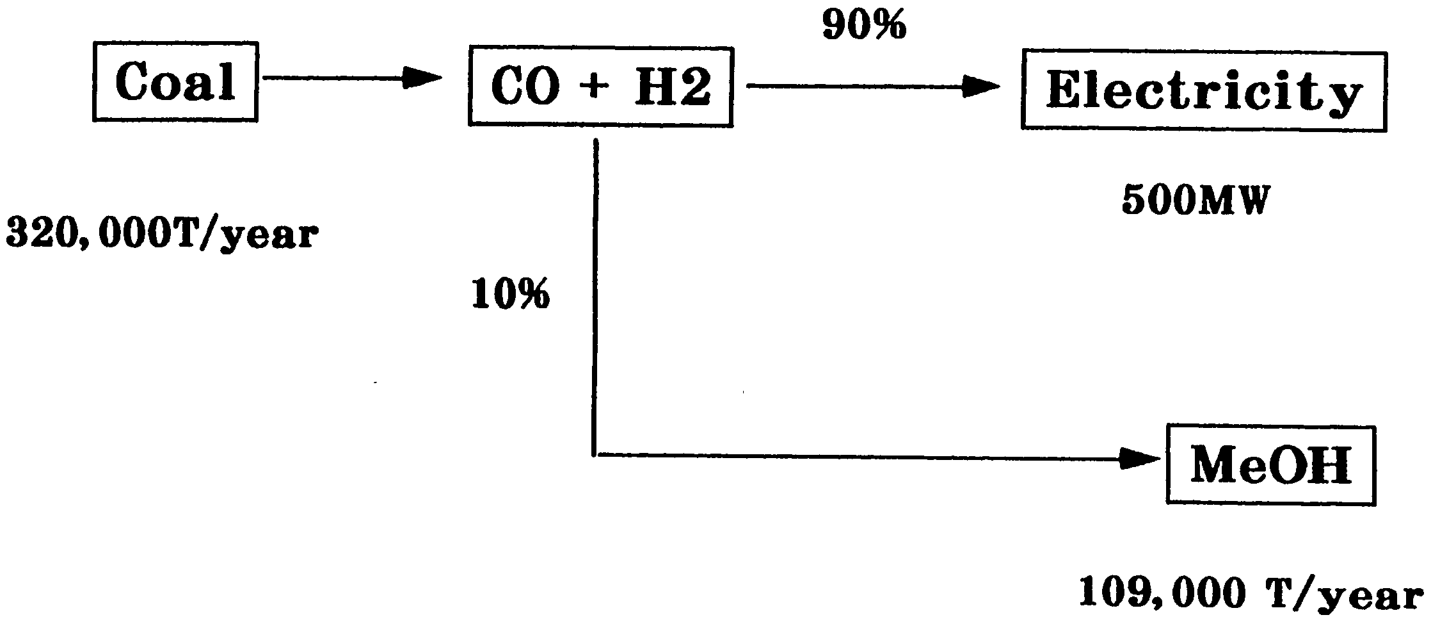

Figure 3. Integrated gasification combined cycle

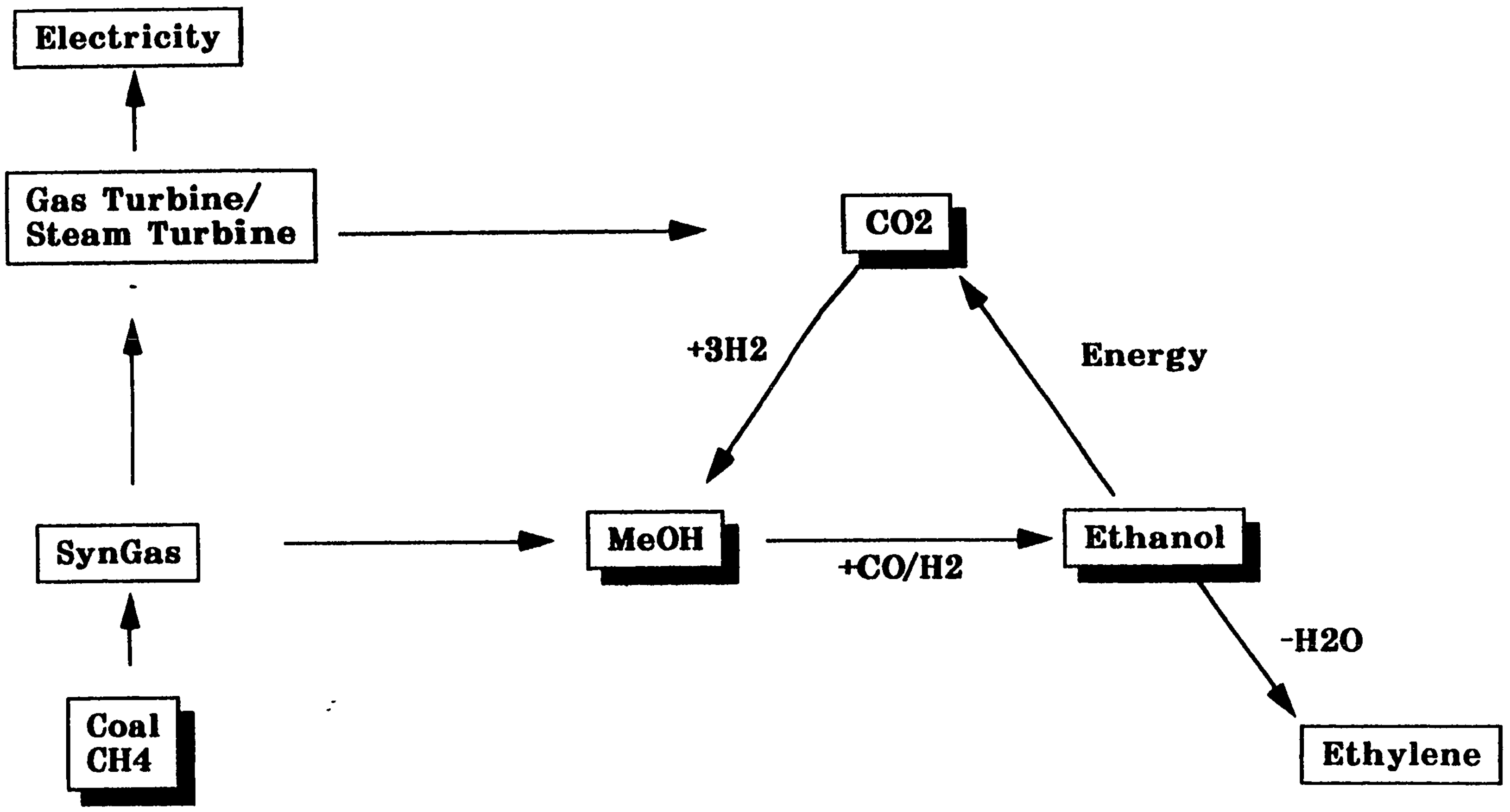

Figure 4. Future energy and chemicals digram based on CO_2, H_2 and CO.