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On the Production of Liquid Synthetic Motor Fuels

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Because of the current increase of the energy consumption, (in particular in the field of transports) and of the necessity of reducing greenhouse gas emissions, it could be interesting to produce liquid synthetic motor fuels, Among the various possibilities of synthetic motor fuels, the methanol appears to be the most promising.

We examine the various ways to produce some ethanol from the steam natural gas reforming. This operation produces some syngas (CO+H_2), which can be then transformed into ethanol following diverse processes of which we compare the advantages and the inconveniences. From the point of view of the energy efficiency we find that syngas direct conversion to ethanol has relatively highest energy ratio than other processes. We propose suitable modifications to improve the yield and selectivity for ethanol.

1. Introduction

Currently, the technologies of CO_2 sequestration (De Castro et al., 2010; Gonzalez-Garza et al., 2009) are the primary means for the mitigation of greenhouse gas accumulation. However, it does not meet world's expectations in terms of safety and costs and no one can be sure about the potential influences of buried CO_2 on the ecosystem in the long term. Conversion of CO_2 instead of its sequestration is presently being explored as one potential alternative solution. Production of liquid synthetic motor fuels appears to be promising (Abidin et al., 2011). In fact, transports contribute to approximately 19% of the world consumption of energy and approximately to 23 % of carbon dioxide (CO_2) emissions and these proportions will increase probably in the future. According to current trends, transport energy use and CO_2 emissions are projected to increase by nearly 50 % by 2030 and more than 80% by 2050 (IEA, 2009)

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All transport modes will need to significantly reduce their emissions in every region of the world. The use of ethanol can reduce carbon dioxide (CO_2) emissions (IEA, 2009). The production of ethanol increased a lot during the last decade until to reach the value of 45.4 Million m^3/year in 2009 (US Senate, 2007), as shown in the Figure 1. The Energy Independence and Security Act (EISA) of 2007 (US Senate, 2007) set a target for ethanol production of 136.3 million m^3 by 2022.

2. Various Pathways for the Ethanol Production

2.1 Syngas from Natural Gas Steam Reforming

The main step of the natural gas steam reforming is the reaction of methane with steam, at 750-800°C (Spath and Mann, 2001). This produces a synthesis gas (syngas), a mixture of hydrogen (H_2) and carbon monoxide (CO) with proportions of 3 H_2 for 1 CO.

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2.2 Syngas Conversion to Ethanol: Various Processes

Syngas can be converted into ethanol and higher alcohols, as shown schematically in Figure 2 and Table 1.

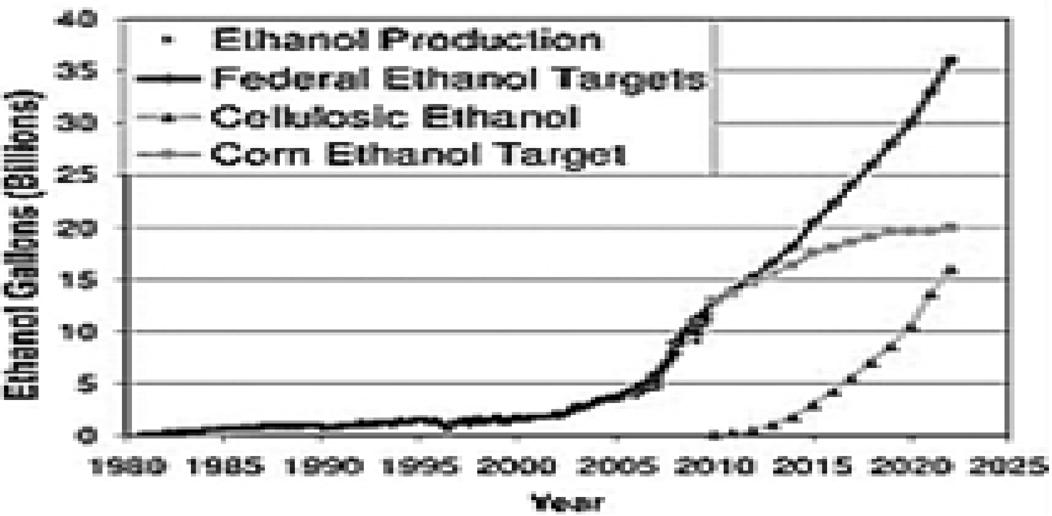

Figure 1: Ethanol production and targets for future (IEA, 2009)

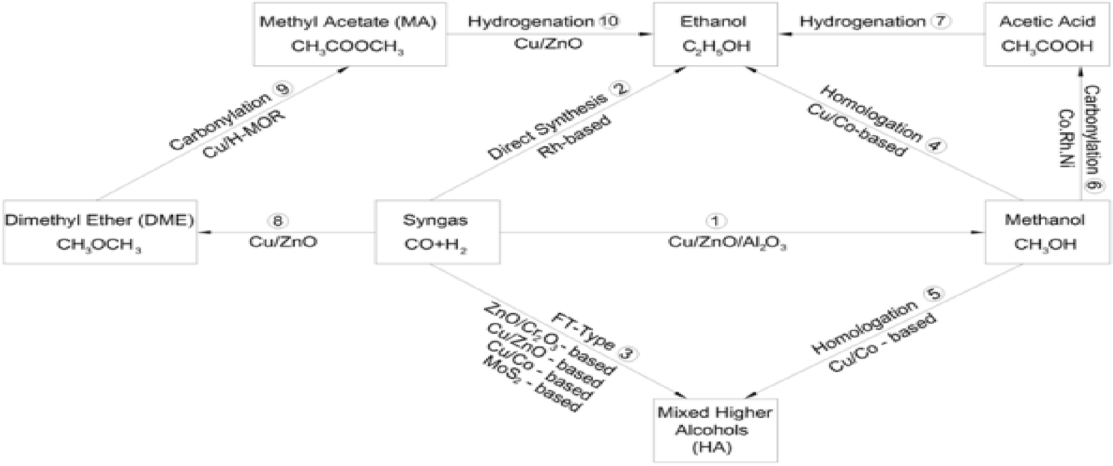

Figure 2: Various Pathways for the conversion of syngas to ethanol and mixed alcohols.

Table 1: Reaction for Various Pathways

$CO(g)+2H_2(g) \rightarrow CH_3OH(g)$ (methanol synthesis)	R(1)
$2CO(g) + 4H_2(g) \rightarrow C_2H_5OH(g) + H_2O(g)$ (direct ethanol synthesis)	R(2)
$nCO(g) + 2\,nH_2(g) = C_nH_{2\,n\,+\,1}OH\,(g) + (\,n - 1)\,H_2O(g)$ (direct HA synthesis)	R(3)
$CH_3OH\,(g) + CO\,(g) + 2H_2\,(g) \rightarrow C_2H_5OH\,(g) + H_2O\,(g)$ (methanol homologation)	R(4)
$C_nH_{2n-1}OH(g)+CO(g)+2H_2(g) \rightarrow CH_3(CH_2)_nOH(g)+H_2O(g)$ (HA homologation)	R(5)
$CH_3OH(g) + CO(g) \rightarrow CH_3COOH(g)$ (acetic acid formation)	R(6)
$CH_3COOH(g) + 2H_2(g) \rightarrow C_2H_5OH(g) + H_2O(g)$ (acetic acid hydrogenation)	R(7)
$3H_2(g) +3CO(g) \rightarrow CH_3OCH_3\,(g)+CO_2(g)$ (dimethyl ether formation)	R(8)
$CH_3OCH_3\,(g)+CO(g) \rightarrow CH_3COOCH_3(g)$ (methyl acetate formation)	R(9)
$CH_3COOCH_3(g) +2H_2\,(g) \rightarrow CH_3CH_2OH(g)+CH_3OH(g)$ (methyl acetate hydrogenation)	R(10)

For the direct conversion of the syngas to ethanol and higher alcohols, Rh-based catalysts give the best ethanol selectivity (Hu et al., 2007), albeit the CO conversion is not optimal. Modified Fischer–Tropsch catalysts (modified FT synthesis catalysts are generally straight-chain primary alcohols.) give moderate ethanol selectivity but methane formation is dominant and methanol selectivity is high (Sugier and Freund, 1998). Syngas transformation to Dimethyl ether (DME) followed by conversion to methyl acetate (MA) and synthesis to ethanol (pathway R8 +R9 +R10 in Table 1), can provide elevated maximum conversion of DME (Yang et al., 2011). This proposed process had a high ethanol selectivity and productivity. Moreover, methanol can be captured as a co-product.

3. Energy calculation for Various Pathways

The relationship between standard heats of reaction ($\Delta H_f^{\ominus}$, KJ) is given by the equation (1):

$$\Delta H_f^{\ominus} = \sum \Delta H_{f\ ,products}^{\ominus} - \sum \Delta H_{f\ ,reactants}^{\ominus} \qquad (1)$$

where $\Sigma \Delta H_f^{\ominus}{}_{prod.}$ is the sum of the enthalpies of products (KJ) and $\Sigma \Delta H_f^{\ominus}{}_{react..}$is the sum of the enthalpies of reactant(KJ).

The heat of combustion of a compound $-\Delta H_c^{\ominus}$ (KJ) is the standard heat of reaction for complete combustion of this compound; it can be calculated through equation (2)

$$-\Delta H_c^{\ominus} = m \times LHV \qquad (2)$$

where m is the mass (kg) and LHV is the lower heating value (KJ/Kg)

3.1 Work of Process

Efficiency of thermal power

Following Ekbom et al. (2005), we assume for the energy efficiency (**η**) of a conventional thermal power station, a value **η**=40%. Then, we can achieve equation (3)

$$W = 0.4H_f^{\ominus} \qquad (3)$$

where W (KJ) is the need of mechanical and electric energies

Efficiency of an ethanol engine

Following (Brusstar and Bakenhus, 2008), the efficiency of an ethanol engine could be: η_1=40%. Then, we achieve equation (4)

$$W_1 = 0.4H_c^{\ominus} \qquad (4)$$

where W_1 (KJ) is the work of the engine and $\Delta H_c^{\ominus}$ is the heat of products combustion

3.2 Application to the Various Pathways

We have calculated the heats of Formation and the Electric Energies for the various pathways for the manufacture of the ethanol. We report the results in Table 2.

Table 2: Heat of Formation and Electric Energy for Various Processes

Pathway No.		Heats of formation	Energy needs (electric)
		$\Delta H_f^{\ominus}$(KJ)	W(KJ)
R2		-252.72	
R1+R4		-252.72	
R3		-1715.93	
R1+R5		-1411.78	
R1+R6+R7	R1	-51.43	
	R6	-211.23	
	R7	9.94	3.98
R8+R9+R10	R8	-246.36	
	R9	-120.39	
	R10	18.19	7.27

Similarly, we report in Table 3 the results of our calculations for the heats of combustion of products and the works of an engine for the various processes.

Table 3: Heat of Combustion of Products and Work of Engine for Various Processes

Pathway No.	Heats of combustion	Work of engine
	$\Delta H_c^{\ominus}$(KJ)	W_1(KJ)
R2	-1327.79	-531.12
R1+R4	-1189.78	-475.92
R3	-3806.35	-1522.54
R1+R5	-1292.39	-516.95
R1+R6+R7	-1327.79	-531.12
R8+R9+R10	-1965.55	-786.22

3.3 Energy Ratio Calculations

The energy analysis is summarized in the diagram shown in Figure 3.

An exothermic reaction produces some heat, but depending of the temperature, it is not so easy to make use this heat, so it has been neglected in our calculations. Our calculations for the energy ratios of the various pathways are reported in Table 4:

Table 4: Energy Ratios for the various pathways

Pathway No.	Input energy	Output energy	Energy ratio
	Q_1(KJ)	Q_2(KJ)	Q_2/Q_1
R2	-1020.84	-531.12	52.0%
R1+R6+R7	-1024.81	-531.12	51.8%
R3	-3062.51	-1522.54	49.7%
R1+R4	-1020.84	-475.91	46.6%
R1+R5	-1131.26	-516.95	45.7%
R8+R9+R10	-2048.95	-786.22	38.4%

The decreasing order of the values of the energy ratios is R2 > R1+R6+R7 > R3 > R1+R4 > R1+R5> R8+R9+R10.

4. Conclusion

We conclude that syngas direct conversion to ethanol and mixed alcohols has relatively highest energy efficiency. The result of the whole process using no-noble catalysts is 49.7%. In calculating the external energy efficiency, the energy content of the syngas is included but not the energy content of the natural gas. This result is an optimistic value, although the results of experiments are somewhat higher than that of industrial plants.

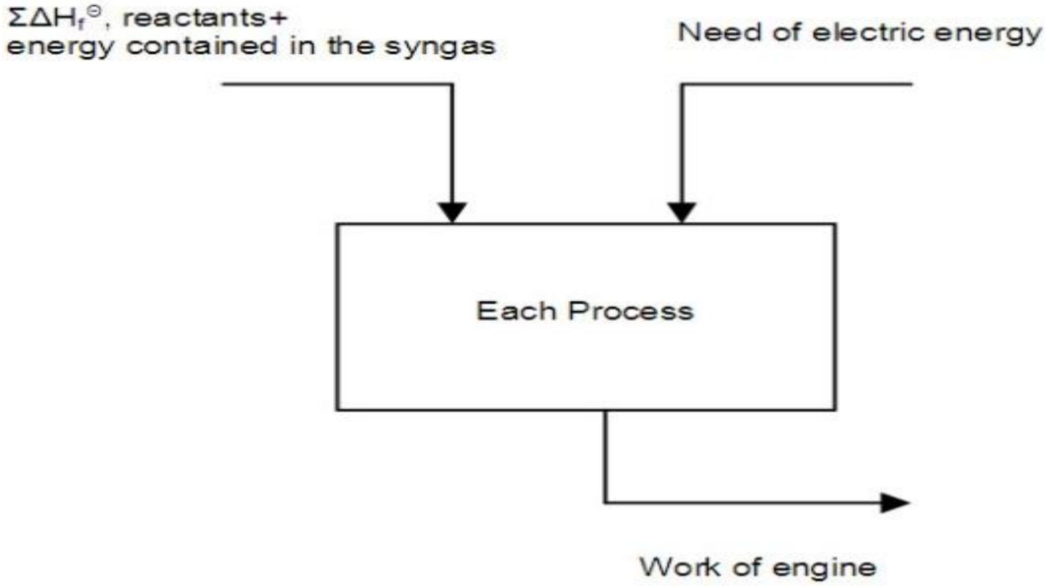

Figure 3: Energy Balance for Each Pathway

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