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Thermodynamic analysis of glycerol conversion processes

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Abstract

The disastrous effects of fossil fuels have been widely recognized in terms of global warming and other environmental degradation phenomena on the Earth. Biomass is now explored as a safer alternative to the non-renewable fuels. In this respect, glycerol has received much attention because of its abundant availability as a by-product from biodiesel industry. About 100 kg of glycerol is generated for every ton of biodiesel produced. With the rapid growth of biodiesel industry all over the world, a large surplus of glycerol is available. Crude glycerol cannot be used as a fuel directly. Further, the purification of crude glycerol is expensive and cumbersome. However, chemistry wise, glycerol is amenable to its transformation into usable fuels and chemicals, as it contains higher number of hydrogen atoms per molecule compared to other fuel-based raw materials like bioethanol. In order to make biodiesel production cost-effective, it has become necessary to find technologies for the value-addition of this by-product. Newer pathways have been developed for the production of high-tonnage value-added chemicals from glycerol [1] in place of traditional low tonnage products, as the latter cannot meet the existing production capacity.

Typical reactions to produce valuable compounds from glycerol include: reforming, partial oxidation, hydrogenolysis, esterification and dehydration. Catalytic reforming is one route for the production of hydrogen from glycerol [2]. Several modifications of reforming are in practice which include steam reforming, aqueous phase reforming, partial oxidation, autothermal reforming and dry reforming. Glycerol oxidation produces compounds such as dihydroxyacetone, glyceric acid, hydroxyl-pyruvic acid, meso-oxalic acid and tartronic acid. Hydrogenolysis of glycerol is a reduction process occurring in presence of hydrogen to give 1,2-propanediol, 1,3-propanediol and other products like 1-propanol, 2-propanol and ethylene glycol [3]. Glycerol dehydration on acidic solid catalysts gives acrolein, a valuable intermediate used in the production of acrylic acid and glutaraldehyde. Glycerol tertiary butyl ether can be derived from glycerol by its esterification. Reaction of glycerol with halogen compounds gives products like 1,3-dichloropropanol, which is an intermediate in

epichlorohydrin synthesis. Synthesis gas produced from glycerol can be used in the preparation of a good number of chemicals. The H_2/CO mixture, not containing any oxygen impurities, can be utilized in Fischer-Tropsch reactions.

In all the processes aimed at identification of new routes the theoretical thermodynamic analysis comes handy. Thermodynamic analysis helps identify the best operating parameters; establish conditions for maximizing the required product; optimize the composition of the product as in the case of syngas; minimize methane and solid carbon formation apart from arriving at the right methodology by comparing the processes technically as well as economically. The present review highlights the important observations made in several thermodynamic analyses in the area of glycerol conversion. The various methodologies adopted during the analyses are also discussed. In appropriate cases comparisons are drawn between the theoretically predicted and the experimental results.

References:

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