CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented in this dissertation report entitled **"**SELECTIVE HYDROGENOLYSIS OF GLYCEROL TO 1, 2-PROPANEDIOL OVER ACTIVATED CARBON SUPPORTED Cu-Ni MONOMETALLIC AND BIMETALLIC NANOPARTICLE CATALYSTS**"** in the partial fulfillment of the requirement for the award of the degree of Masters of Technology in Chemical Engineering with specialization in "Industrial Pollution Abatement" is an authentic record of my own work carried out during the period from June 2013 to June 2014 under the supervision of Dr. Prakash Biswas, Assistant Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee.

The content in the report has not been submitted by me for the award of any other degree of this or any other Institute/University.

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This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief.

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A dissertation or any publication can reach to the acme only by the proper guidance, cooperation and kind words of the individuals involved.

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ABSTRACT

Decline of fossil fuel reserves and increase of fuel prices prompted the global oil industry to look for an alternative from renewable sources. Biodiesel is one such option and it is produced from animal fats and vegetable oils and has become more attractive because it is more environmentally friendly. One of the most important byproducts of biodiesel industry is glycerol. 1 kg of crude glycerol is formed for every 9 kg of biodiesel produced. As a result, there is surplus of the by-product glycerol. This glycerol can be converted to value added products like propanediols etc. to generate revenue for biodiesel industry. Hydrogenolysis of glycerol to 1, 2-propanediol is one of the processes of transformation of glycerol. 1, 2-propanediol is a nontoxic and high-demand chemical, which is extensively used for polyester resins, food products, antifreeze, liquid detergents and pharmaceuticals etc.

The main objective of this work was to study the catalytic performances of Cu-Ni based activated carbon supported monometallic and bimetallic catalysts during vapor phase hydrogenolysis of glycerol to 1, 2-propanediol. The catalysts were prepared by incipient wetness impregnation method by taking various Cu-Ni ratios (3, 1 and 0.33). The characterization of the catalysts was done by various techniques such as BET surface area, X-ray diffraction, TPD-NH_3 measurements and scanning electron microscopy (SEM). The surface area and pore volume of activated carbon support are 643m^2/g and 0.306cm^3/g, respectively. Surface area of the Cu-Ni/AC catalysts having different metal loading is in range of 147-468 m^2/g. The surface area for Ni/activated carbon is highest (468 m^2/g) whereas Cu/activated carbon has shown the lowest surface area (147 m^2/g). XRD patterns showed the formation of NiO and CuO peaks over the surface of activated carbon support. NH_3-TPD profile showed the presence of strong acidic sites for all the prepared catalysts. Hydrogenolysis of glycerol was carried out at fixed reaction conditions of 220^{o}C temperature and 7.5MPa H_2 pressure with an aqueous glycerol solution (20 wt %) used as feed. 1, 2-propanediol and acetol were the major product of glycerol hydrogenolysis. The catalytic performance of Cu-Ni (1:1)/AC catalyst was the best among the catalysts used for the hydrogenolysis reaction with a glycerol conversion of 91% and 1, 2-PDO selectivity of 61.23%. Other bimetallic catalysts Cu-Ni (3:1)/AC and Cu-Ni (1:3)/AC gave a glycerol conversion of 81% and 90.5% with selectivity to 1, 2-PDO58.4% and 64.1%

respectively. The selectivity to 1, 2-PDO with all catalysts varies in the range of 27.8-64.3%. Acetol was also formed in the range of 31.5-61.2%. The glycerol conversion increases with increase in reaction temperature as predicted earlier. The conversions recorded were highest (97.45-99.3%) at 260^{o}C as compared to conversions at other temperatures. High temperature favors glycerol conversion but selectivity to 1, 2-PDO was highest (79-86%) at 240^{o}C. Selectivity to acetol was increased from 11.2-16.5% at 240^{o}C to 23.7-27% at 260^{o}C.

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