EXECUTIVE SUMMARY

Climate change caused by the extensive use of fossil fuels is currently one of the most challenging issues for scientific communities and nations across the world. The population of many countries is growing rapidly and it is expected the world population to reach approximately 8.5 billion by the year 2030. At the same time, there is a spike in the economic development, especially in developing countries like China and India and these countries have entered their most energy intensive phase of economic growth. With increase in population, the demand for energy, food and natural resources will increase substantially over the next decade. Thus, an important issue faced today is to meet the increasing energy demand and have sustainable energy resources for the future use while protecting the environment.

Bioenergy can play a major role in the industrial countries consuming huge amount of fossil energy and are also responsible for increasing CO₂ level. The rising world energy demand, uneven distribution of fossil resources and their continuous depletion along with adverse impact on the environment, urge many countries to formulate policies to promote sustainable energy source. The Energy Independence and Security Act (EISA) of 2007, United States (US) defined a number of mandates with respect to renewable fuels. One of these mandates called for the production of 16 billion gallons of cellulosic fuel by the year 2022. In the US, one of the policies to promote biofuels is described by the Renewable Fuel Standard (RFS) that dictates to increase the current biofuel usage from 7.1 to 15% in transportation fleets. Similarly, European Commission (EC) in 2007 mandated that out of total energy use, 20% needs to be achieved from renewable sources and out of that, 10% to be used in transportation by 2020 [20]. Government of India in 2009 mandated 5% ethanol blending in gasoline and has an ambitious plan to reach up to 20% blending by 2017. The current ethanol production is India is based on sugarcane molasses and in order to meet the set target extensive research and development efforts are undergoing to commercialize the cellulosic ethanol technology.

United States Environment Protection Agency (USEPA) has classified the biofuels based on their GHG emission reduction capability as compared to gasoline. In this category only those fuels are considered as advanced biofuels which reduces the GHG emission more than 60% and each biofuel has assigned distinct identification number and specific GHG reduction target. Each biofuel has specific GHG emission reduction mandate such as 20% for corn ethanol, 50% for sugarcane and 60% for cellulosic ethanol. Thus, it is not sufficient to produce the biofuel, but the produced fuel must meet the minimum legislated GHG reductions. In the US and the Europe, financial incentives are extended only to those biofuels that meet GHG reduction criteria and India is also likely to follow the same practice. Therefore, it is essential to conduct the life cycle assessment (LCA) of the biofuels production process. LCA is a tool to quantify and assess environmental aspects associated with a product, process or service through its life cycle.

The production of biofuels is classified into three categories: first, second and third generation. The first generation biofuels are produced directly from the fermentation of sugars present in biomass to ethanol using a fermenting yeast *Saccharomyces cerevisiae*. The second generation biofuels production is a tedious process that first involves pretreatment to break down lignin and release cellulose and hemicellulose from the cell wall of biomass. Next step is the hydrolysis of the cellulose using cellulase enzymes followed by the fermentation. Third generation biofuels are produced from algae or any other advanced technology.

The extensive literature survey revealed that there are several published literature for sustainability assessment of ethanol in different countries of the world. However, hardly any studies were published/ or reported on the sustainability assessment of ethanol in India. LCA in itself is a new concept in the country and a lot of emphasis is now being given particularly in assessing sustainability of product/process and service. In order to address the mentioned research gaps especially for sustainability of ethanol as a biofuel, thesis aimed to conduct the LCA of fuel ethanol derived from sugarcane molasses, i.e. 1G ethanol

and rice straw, i.e. 2G ethanol in India using different production technologies. LCA was conducted for 1 ton of fuel grade ethanol production from sugarcane molasses in the northern region (NR) and western region (WR) of India. Maharashtra in WR and Uttar Pradesh in NR was selected for analysis as these are two largest sugar cane producing states and also have largest number of sugar refineries in India. The impact of regional differences in agro-practices, sugarcane yield, sugar content and technical variations were analyzed on overall fuel ethanol LCA results. The system boundary for this study was based on the latest technologies available and included the following unit processes: sugar cane farming, sugarcane transport, sugar production, molasses transport, ethanol production, ethanol transport, blending and combustion in automobiles. In this study, most of the data use was secondary, obtained from various technical reports, government reports, websites, sugar industry reports and literature. However, due to limited availability of secondary data at various steps, primary data was obtained from personal communication with experts at National Sugar Institute (NSI), Kanpur and Vasantdada Sugar Institute (VSI), Pune. These institutes have a collection of data from local sugar-cane farmers and almost all sugar mills of different regions in India

Various allocation approaches such as: without allocation (WA), mass allocation (MA), energy allocation (EA) and market price allocation (MPA) were used to distribute emissions and energy consumption between product and co-products. GHG emissions reduction with respect to gasoline ranged from 68.4-75.9% in the NR and 69.6-75.8% in WR. Similarly, the net energy ratio (NER) also varied with different allocation approaches and ranged from 0.38 to 3.39 in the NR and 0.48 to 4.23 in WR. Using MA approach, maximum GHG emissions reduction of 75.9% and 75.8% and NER of 3.39 and 4.23 in NR and WR respectively were obtained. The LCA results of 1G ethanol established the environment friendly and energy benefits of ethanol production and use with respect to gasoline. LCA was further extended to study environmental and energy benefits of ethanol blending programme (EBP). Using MA, E5 blend in NR gave

GHG emission reductions of 4.27%, slightly higher than 4.22% in WR and E10 blend gave 8.55% and 8.44% in NR and WR respectively. NER of gasoline in E5 and E10 blends increases from 0.80 to 0.94 and 1.08 in NR and to 0.98 and 1.15 in WR using MA approach.

Rice straw, a by-product of rice is the most abundant lignocellulosic agricultural residues in most Asian countries. It has been identified as a potential feedstock for making ethanol as it contains 35-40% cellulose, 17-25% hemicelluloses and 10-20% lignin apart from some amount of extractives and silica. These polymeric carbohydrates (cellulose and hemicellulose) can be hydrolyzed to monomer sugars (glucose, xylose, and galactose) by the action of chemicals, enzymes and further converted to ethanol using Saccharomyces *cerevisiae*. However, due to recalcitrant nature of biomass, extracting sugars from these residues poses challenges and hence, pretreatment is an essential step in biochemical conversion pathway as it hydrolyzes structural carbohydrates into sugar monomers. During pretreatment, the protective layer of lignin from the biomass is broken down and this makes polymeric carbohydrates more accessible to enzymes. The main aim of pretreatment is to improve overall sugar recovery as ethanol yield is dependent on the effectiveness of pretreatment method. There is a wide range of pretreatment methods used for producing cellulosic ethanol and are broadly classified in four categories: physical (milling, grinding), physicochemical (microwave, steam explosion, ammonia fiber explosion), chemical (ozonolysis, dilute acid) and biological (fungal degradation).

Indian Oil Corporation Limited (IOCL), R&D Centre, Faridabad has set up a pilot facility of processing 250 kg/day lignocellulosic biomass in the year 2012. The characteristic feature of IOCL cellulosic ethanol technology is that biomass is initially milled to a particular size, soaked in dilute acid and then structure is broken with steam using two diverse pretreatment technologies of dilute acid (DA) and steam explosion (SE). Both the pretreatment technologies have different set-up in two distinct plants and operate at different temperature. The mechanism of solubilizing C5 sugar from the hemicellulose in liquid hydrolysate is different in both the pretreatment. After pretreatment, the solid obtained in the form of slurry, predominantly having C6 sugars are directly used for enzymatic hydrolysis to obtain monomeric sugars. The C6 and C5 monomers are then co-fermented using yeast strain to produce ethanol. The leftover lignin and holocellulose residues are burnt internally in co-generation plant to produce electricity. The energy requirement of the plant is met up by internal bioelectricity, and surplus electricity is sold to the grid that displaces coal based electricity. The waste water generated during the process is anaerobically digested for production of biogas. After evaluating LCA of 1G ethanol, environmental sustainability of 2G ethanol from rice straw using two diverse pretreatment technologies of DA and SE was conducted. The system boundary consisted of following unit processes: biomass collection, biomass transport, pretreatment, enzymatic hydrolysis, fermentation, distillation and dehydration, ethanol blending, distribution and end use. The ethanol produced from the processing of 1 ton straw was the reference flow of the study and while comparing the results with gasoline as a reference system, 1MJ of transportation fuel was chosen as the functional unit. Since, rice straw is a waste and is not a main crop; therefore, agriculture phase was not included in study. The data used in study was collected from various government reports, personal communication with experts, experiments conducted at the laboratory and NREL reports.

Using DA and SE, the ethanol yields from the processing of 1 ton straw were 239 and 253 L and life cycle GHG emissions were 292 and 288 kgCO₂eq./ton straw respectively. The net energy input during the life cycle of ethanol was 1736 and 1377 MJ/ton straw in DA and SE respectively. The major GHG emissions and energy benefits were obtained using lignin produced in the plant to generate electricity resulting in displacement of the coal based electricity. Enzyme production and its use were identified as GHG emission and energy consumption hotspot in the ethanol production process. While comparing the results with gasoline, DA and SE resulted in a reduction of 77 and 89% GHG emissions and NER of 2.3 and 2.7 respectively. A series set of experiments varying feedstock, acid concentration; reaction time and temperature have been performed at IOCL pilot plant for ethanol production. The key results from optimized conditions revealed that DA method resulted in the formation of inhibitory compounds and pseudo lignin along with burden of unnecessary materials like ash, extractive, lignin or their condensed products. Hence, reduces the conversion efficiency of cellulose to monomer sugars and results in input of higher enzyme dose to achieve the desired hydrolysis efficiency. LCA results based on these pilot scale experiments data showed that ethanol resulted in reduction of 76% GHG emissions as compared to gasoline. However, LCA results revealed that the enzyme production is the GHG emission hotspot in ethanol production. Therefore, in order to address the above mentioned issues, there was a need to improve the pretreatment process in a way that reduces the enzyme doses and gives higher ethanol yield and at the same time lower the emissions and consequently could reduce the ethanol cost.

The next study analyzed the series of extraction process including water and varying alkali concentrations followed by DA pretreatment, enzymatic hydrolysis and fermentation to produce ethanol. In extraction process, significant amount of unwanted materials were removed, comprising of extractives, partly lignin and ash. This new process termed as modified pretreatment (MP), is a strategy to reduce the enzyme dosage and have higher yield of sugars. In line with this, further aim was to assess the sustainability of the process from an environment and economic perspective. LCA and life cycle costing (LCC) results would give real insight on emissions and economic benefits by comparing different MP scenarios with conventional pretreatment (CP). By using water (MP1) and 0.2 (MP2), 0.4(MP3) and 0.5% (MP4) concentration of alkali in soaking media, ethanol production was 242, 256, 262 and 267 L as compared to 218 L in CP. The introduction of extraction step prior to DA pretreatment fulfills the objective of reducing enzyme dosage by 23, 27, 34 and 39% in MP1, MP2, MP3 and MP4 respectively. However, use of alkali had negative impact on environmental emissions. Overall, MP1 using water as a soaking media for

extraction had GWP (-0.58 kg CO₂ eq./L), EP (0.7×10^{-4} kg PO₄ eq./L), AP (- 6.8×10^{-3} kg SO₂ eq./L), POCP (0.1 kg C2H6 eq./L) and is the most environmentally suitable pretreatment process for ethanol production in respect to other scenarios.

Besides conducting the LCA of cellulosic ethanol by using CP and MP, the study was further extended to compare the LCA of other rice straw utilization practices, since open burning of straw in the field is a serious environmental hazard. Therefore, efficient utilization of rice straw can solve the issues of rice straw management. LCA was conducted for four most realistic utilization practices: (1) straw incorporated into the field as fertilizer (2) use as an animal fodder (3) use for electricity production and (4) use for biogas production and then compared with ethanol production. Among all the practices, utilization of rice straw for electricity production resulted in highest benefits in GWP, AP and POCP followed by ethanol and biogas production. However, in order to replace transportation fuel, a liquid fuel like ethanol can serve the better option in present automobile sector. Similarly, to replace fossil based liquefied petroleum gas (LPG) it is necessary to produce biogas. Moreover, India energy basket is a mix of liquid and gaseous fuel as given in Chapter 1. Hence, it is necessitated to take firm decision before diverting straw for electricity production.

Most researchers explained that biofuels are carbon neutral as CO_2 emitted during use phase of ethanol is sequestered by plants in next cultivation cycle. However, this thesis underline that this concept is just a myth in scientific field and there are fossil based carbon emissions at each step of ethanol production. These emissions should not be ignored in life cycle of biofuels. The thesis gave real insight on the environmental and energy benefits of biofuel in India. The environmental evaluation of the life cycle of ethanol produced from sugarcane molasses and rice straw using different technological approaches meet the standard GHG emission reduction criteria as compared to gasoline. The intended audience of this thesis is policy makers, private investors, researchers and other stakeholders who are interested and motivated enough to consider making concerted and unified efforts toward the production of sustainable biofuels in developing countries. The insight provided in this thesis could help national/regional governments and international development organizations to accelerate the development agenda on the promotion of bioenergy services needed for transition to a low carbon development path.