

## **CHAPTER 2**

### **REVIEW LITERATURE**

Bibliographic survey was conducted to develop the understanding in the area of sustainability assessment of first (1G) and second generation (2G) ethanol and is divided into three sections. First section provides background on previous LCA studies of fuel ethanol from sugarcane juice and molasses. Second section describes LCA studies on second generation ethanol, comparing different pretreatment technologies, energy and economic analysis of cellulosic ethanol. GHG emissions and energy hotspots were identified in the life cycle of fuel ethanol. The last section deals with the analysis of environmental impact of different rice straw utilization practices. The review literature in thesis has been restricted to last 10 years.

## 2.1 LCA STUDIES OF FIRST GENERATION (1G) ETHANOL

Brazil had a long history of producing ethanol directly from sugarcane juice. Several authors have analyzed sustainability of fuel ethanol from sugarcane juice in Brazil [49-53].

Smeets et al., 2008 [49] showed that average NER of fuel ethanol in Brazil is 4.7-7.8. However, due to difference in sugarcane yield, ethanol yield, generation of electricity and choice of reference system a range of NER can be obtained. In worst case it was 5.5 and that can reach upto 10.6 in best case. Average GHG emissions calculated were 370-396 kgCO<sub>2</sub>eq.m<sup>-3</sup> ethanol and in worst case when, there is no co-generation facility GHG emissions were 498 kgCO<sub>2</sub>eq.m<sup>-3</sup>. The emissions can further reduced to a maximum of -821 kgCO<sub>2</sub>eq.m<sup>-3</sup> in case when there is full mechanical harvesting and instead of burning the residues, they are diverted for gasification along with cogeneration.

Luo et al., 2008 [51] compared LCA of fuel ethanol production for two scenarios. (1) ethanol from juice and (2) ethanol produced both from juice and bagasse whereas electricity is produced from lignin residues. The FU was 1 km distance to be travelled from midsize car. The results showed that GHG emissions from gasoline were 0.24 kgCO<sub>2</sub>eq./FU that reduced to 0.18 and 0.08 kgCO<sub>2</sub>eq./FU respectively using E10 and E85. The results were further improved in each environmental category in future case as the amount of ethanol produced from sugarcane increased.

Macedo et al., 2008 [52] evaluated the GHG emissions and energy balance during production of ethanol from sugarcane. Two ethanol production scenarios were studied: in year 2005/2006 as a base case, and another in year 2020 as a proposed conservative scenario. With development in technologies net energy ratio (NER) from 9.3 in 2005/2006 would reach 11.6 in 2020 and GHG emission would reduce from 0.44 to 0.34 kgCO<sub>2</sub>eq.L<sup>-1</sup> ethanol in the 2020 scenario.

Goldemberg et al., 2008 [54] studied the sustainability of sugarcane based ethanol and concluded the positive impacts of ethanol in reducing CO<sub>2</sub> emissions and lower requirement of fossil energy during production. The removal of lead compounds and reduced NO<sub>x</sub> emissions with respect to

gasoline make ethanol a sustainable fuel in Brazil. The authors reported average NER of 8.3 and GHG emissions of 389 kgCO<sub>2</sub>eq.m<sup>-3</sup> ethanol.

Nguyen et al., 2008 [55] analyzed environmental and economic impacts of fuel ethanol from cane molasses in Thailand. The FU was 673 km distance travelled by gasoline (50L) and E10 (50.6L) fuelled vehicle. The results showed that fossil energy use in gasoline and E10 was 1929.3 and 1776.3 MJ (7.93% less) respectively. The GHG emissions using E10 blend were 138.27 kg, 7.51% lower while using gasoline (149.49 kg).

Nguyen et al., 2008 [56] studied energy use in producing molasses based ethanol in Thailand. The system involved three unit processes: sugarcane cultivation, molasses and ethanol production. When system co-products are not utilized for energy, negative NEV is found for ethanol whereas a positive net energy balance of 5.95 MJ.L<sup>-1</sup> is obtained when co-products are utilized. The results also revealed that 1 MJ of fossil inputs can produce 6.12 MJ of ethanol fuel. E10 blend consumed 5.3% less fossil energy and had a similar impact on acidification as compared to gasoline. The fuel ethanol showed higher impacts in other environmental categories like eutrophication and smog formation as compared to gasoline.

Ometto et al., 2009 [57] analyzed different environmental impact categories for ethanol production in Brazil and reported that even though ethanol is a renewable fuel but consumes a high quantity of fossil energy like diesel during its life cycle. FU was 10,000 km distance travelled by fuel car that corresponds to 1000 kg ethanol use. Total 540 kgCO<sub>2</sub>eq. emissions were produced during ethanol life cycle that corresponded to 74.3% reduction in GHG emissions as compared to gasoline. The following parameters were analyzed as emission hotspots: use of fossil energy during water use in irrigation and at ethanol plant and harvesting of cane.

Khatiwada et al., 2009 [58] estimated cradle to grave life cycle energy analysis and net energy ratio (NER) of 7.8 was obtained, that indicates the renewability of ethanol. Similar results were reported by Seabra et al., 2011 [50] while evaluating GHG emissions and energy use during ethanol producing. They reported NER of 6.5 and GHG emissions as 21.3 gCO<sub>2</sub>

eq.MJ<sup>-1</sup> respectively. Both the studies have identified sugarcane agriculture phase as emission and energy intense process.

Gopal et al., 2009 [59] studied the environmental and economic impacts of ethanol production by exporting molasses from Brazil in California. GREET model is specific to assess sustainability of US transportation fuels and basically lack sugarcane based production pathways. Authors modeled ethanol manufactured from molasses, keeping all other processes and inputs similar to Brazilian conditions. The modeled life cycle GHG results were 15.1 gCO<sub>2</sub>eq.MJ<sup>-1</sup> which were lower than as described in California GREET model (26.6 gCO<sub>2</sub>eq.MJ<sup>-1</sup>).

Ngyuen et al., 2010 [60] studied environmental impacts of converting a sugar mill into a biorefinery in Thailand. The authors concluded that it would help in mitigating climate change by production of bio-electricity and fuel ethanol. Improvement in efficiency while producing electricity from bagasse and trash is the biggest advantage to a biorefinery. Furthermore, ethanol production from bagasse in biorefinery is an added advantage. The GHG savings of 14 MTCO<sub>2</sub>eq./year could be achieved when producing ethanol from excess sugar than in Thailand.

Khatiwada et al., 2011 [61] evaluated life cycle greenhouse gas (GHG) balances of molasses based ethanol in Nepal. The total life cycle emissions of ethanol are 432.5 kgCO<sub>2</sub>eq.m<sup>-3</sup> ethanol (i.e. 20.4 gCO<sub>2</sub>eq.MJ<sup>-1</sup>), that corresponds to 76.6% reduction relative to conventional gasoline. He reported that sugarcane yield is a deciding factor in determining GHG emissions. Sale of surplus electricity produced by burning of bagasse can reduce the emissions by replacing coal based electricity.

Silalertruksa and Gheewala, 2011 [62] discussed environmental and socio-economic impacts of ethanol production from cassava and molasses in Thailand. The parameters analyzed were: GHG emissions, employment creation and effect on gross domestic product (GDP). The results revealed that GHG emissions shows variation, depending upon the production, system boundary, allocation approach and consideration of land use changes. GHG emissions for molasses and cassava ethanol ranged between 28-100 and 27-91 gCO<sub>2</sub>eq.MJ<sup>-1</sup> respectively.

Garcia et al., 2011 [63] studied life cycle GHG and energy balance of ethanol production in Mexico using European Renewable Energy Directive (RED) methodology. The system boundary included: agriculture; transport of feedstock to refinery; processing of feedstock in industry and ethanol transport to blending depots. Authors identified that agricultural practices, land use changes, transportation distances, process conversion technologies and method of allocation had significant impact on the LCA results. While producing ethanol directly from juice and generating surplus electricity from bagasse the process resulted in 36.8 gCO<sub>2</sub>eq.MJ<sup>-1</sup> whereas producing ethanol from molasses and electricity from bagasse resulted in 48 gCO<sub>2</sub>eq.MJ<sup>-1</sup>.

Nguyen et al., 2012 [64] studied GHG emissions of molasses based ethanol and using different allocation approaches and system expansion. The results showed that system expansion has highest emissions of 1400 gCO<sub>2</sub>eq.L<sup>-1</sup> followed by 1050 gCO<sub>2</sub>eq.L<sup>-1</sup> in mass and 423 gCO<sub>2</sub>eq.L<sup>-1</sup> emissions in energy allocation.

In an another study, Khatiwada et al., 2012 [53] estimated life cycle energy analysis and results showed positive net energy ratio (NER) of 7.8 indicating the renewability of ethanol. Similar results were reported by Seabra et al., 2011 [50] while evaluating GHG emissions and energy use during ethanol producing. They reported fossil energy use of 80 kJ.MJ<sup>-1</sup> and emissions as 21.3 gCO<sub>2</sub> eq.MJ<sup>-1</sup> ethanol respectively.

Amores et al., 2013 [65] while conducting LCA of sugarcane ethanol in Argentina reported that agriculture is the process that contributes largest to the environmental emissions. During agriculture, large amount of fossil fuel is consumed in irrigation, manufacturing of fertilizers and harvesting. The authors studied three scenarios of ethanol production using different technologies i.e. utilizing molasses, honey and juice obtained from sugarcane processing. The production of 1 kg ethanol from molasses, honey and juice emitted 22.5, 19.2 and 15.0 kg CO<sub>2</sub> respectively.

Chum et al., 2013 [66] compared LCA of Brazilian sugarcane and US corn ethanol production systems. The study provided insights into the characteristics of mature Brazilian sugarcane and maturing US dry mill corn ethanol industries. Both the systems showed improvement in NER over time;

sugarcane system showed NER increased from 7.0 in 2002 to 9.4 in 2009. Similarly, corn system showed improvement from 1.1 in 2000 to 1.7 in 2010. The reason for improvement is integration of combined heat and power plant with ethanol plant by utilizing by-products.

Cavalett et al., 2013 [67] compared the LCA of ethanol with gasoline in Brazil using different LCIA methods such as Eco-indicator 99, ReCiPe, CML 2001, EDIP 2003, Impact 2002+, TRACI 2 and Ecological Scarcity 2006. The emissions between product and by-product were allocated on basis of energy content. The results of all the methods showed that ethanol has lower environmental burden on global warming, ozone layer depletion and fossil depletion. However, ethanol does have a negative impact on other categories like nutrient enrichment, acidification, smog formation and land use. Using ReCiPe method and excluding land use changes ethanol showed better performance than gasoline.

Tsiropoulos et al., 2014 [68] studied LCA of sugarcane ethanol production in India and compared it with Brazil, since these two countries are the largest producer of sugarcane. Environmental impacts were assessed with Impact 2002+ and environmental impact categories like GHG emissions, freshwater eutrophication, ecosystem quality, human health, water use, fossil and energy use. It was found that Indian ethanol ( $0.09\text{--}0.64 \text{ kgCO}_2\text{eq./kg}_{\text{ethanolIN}}$ ) compared to Brazilian ethanol ( $0.46\text{--}0.63 \text{ kgCO}_2\text{eq./kg}_{\text{ethanolBR}}$ ) had lower or comparable GHG emissions and non-renewable energy use ( $-0.3\text{--}6.3 \text{ MJ/kg}_{\text{ethanolIN}}$ ,  $1\text{--}4 \text{ MJ/kg}_{\text{ethanolBR}}$ ).

Mayer et al., 2015 [69] studied LCA of small scale fuel ethanol production (SSEP) in Brazil using Eco-Indicator 99 and CML 2 Baseline 2000 assessment methods. The results revealed that nitrogen and phosphorus rich fertilizers, along with herbicides and limestone, were responsible for the highest emissions in the agricultural sector, while the use of electricity and equipment had the highest impacts in the industrial sector. Overall, the industrial sector showed the highest environmental impacts. The SSEP GWP was  $0.128 \text{ kgCO}_2\text{eq.MJ}^{-1}$  ethanol, which was almost 20 times higher than in large scale ethanol production plant.

Filoso et al., 2015 [70] studied the GHG emissions reduction potential of sugarcane ethanol in Brazil. The authors concluded that LCA results are dependent on agricultural and industrial practices. The environmental impacts on water, air and soil were analyzed. The area of improvement to reduce GHG emissions are: ban on sugarcane burning, reduce water consumption in mills and utilization of by-products. Major improvements regarding prevention of the soil erosion, degradation, protection of water resources against pollution from pesticides and other toxic chemicals are also need to be practiced in future.

Soam et al., 2015 [71] studied the impact of regional difference on LCA of fuel ethanol production. The authors studied ethanol production in Northern and Western regions of India. It was found that due to differences in agriculture and technological practices such as higher sugarcane and sugar yield in northern region, a NER of lower GHG emissions are produced in western region. The results of different ethanol blends were compared with gasoline and it was found that E5 blend give ~4.4% GHG emission reductions as compared to gasoline.

Khatiwada et al., 2016 [72] studied the LCA of ethanol from cane molasses in Indonesia. GHG emissions reported along the lifecycle were 29 g CO<sub>2</sub>eq. MJ<sup>-1</sup> that corresponds to 67% lower emissions than gasoline. NEB and NER estimated were 17.7 MJ/L and 6.1 that shows quiet higher savings in energy than producing gasoline.

Silalertruska et al., 2017 [73] conducted LCA based of sugarcane biorefinery in Thailand. The biorefinery system included sugarcane cultivation, harvesting, milling and by-product utilization i.e. bagasse for steam and electricity, molasses for ethanol and vinasse for fertilizer and soil conditioner. The potential impacts on GHG, ozone formation, acidification, particulate matter formation and fossil depletion could be reduced by around 38%, 60%, 63%, 90%, and 21% respectively as compared to base case where there is no mechanized agriculture and trash is utilized for electricity production.

## **2.2 LCA and LCC STUDIES OF SECOND GENERATION (2G) ETHANOL**

LCA methodology has been extensively applied to assess the sustainability of lignocellulosic ethanol and noted that ethanol contributes significantly to abate GHG emissions and can improve energy security [74-76]. The reduction in GHG emission is reported to be dependent on feedstock, system boundary, conversion technology, efficiency, co-products utilization and allocation methods [77-81]. In LCA studies, system boundaries cause a considerable variation since, it not only depends upon the variant of LCA (e.g. cradle to grave, well to pump, well to well etc.) but also dependant on space and time that can significantly affect GHG balances and energy [82, 83].

Blottnitz et al., 2007 [75] in his review article studied NER of fuel ethanol from different substrates such as sugarcane, sugar beet, corn, corn stover, molasses, wheat straw and bagasse in different countries. The lowest NER of 1.3 was obtained for corn ethanol production in USA and highest NER of 7.9 was for sugarcane ethanol in Brazil. Lignocellulosic residues such as wheat straw, corn stover and bagasse resulted in NER of 5.2, 4.2 and 3.5 respectively.

Crop residues are identified as the most abundant feedstock for lignocellulosic ethanol and have gained an increased attention as a renewable energy source [80, 84-88]. Corn stover has been identified as the most available residue for ethanol production [89-93] and reduces 86–113% of GHG emissions when E85 blend is used in flexible fuel vehicles (FFV) [94-99]. Kim and Dale, 2005 [100], Whitman et al., 2011 [101] reported that corn stover as a feedstock for ethanol has the potential to lower GHG emissions by 50% more than conventional corn-grain ethanol in US.

The allocation method plays a vital role in estimating the emissions and reduction potential as seen in case of corn stover and corn ethanol studied by [100, 102, 103]. The mass and energy allocation approach give higher emissions to ethanol than economic allocation. The reason is that cellulosic biomass is produced in more quantity than agricultural crop but is cheaper [104]. Luo et al., 2009 [104] studied effect of different allocation on LCA results of corn stover ethanol. GWP while traveling 1 km distance from

gasoline was 0.24, 0.22 and -0.14 kgCO<sub>2</sub>eq. using mass, energy allocation and system expansion. However, GWP decreased to 0.08 kgCO<sub>2</sub>eq. while applying mass allocation and increased to 0.36 kgCO<sub>2</sub>eq. in economic allocation for E85 blend. The GWP reduced significantly in system expansion. The reason of higher emissions while moving from mass to economic allocation is due to change in allocation ratio from 1.7 to 7.5 and therefore, higher emissions are attributed to stover.

Garcia et al., 2009 [105] conducted LCA of ethanol derived from mustard stalk and authors found that while moving from gasoline to ethanol based fuels, GWP and fossil energy use were reduced. However, impact on other environmental categories such as POCP, terrestrial and marine eutrophication were increased considerably due to the emissions from upstream processing of ethanol manufacture. For driving 1 km distance, gasoline, E10, E85 and E100 resulted in 0.26, 0.22, 0.16 and 0.14 kgCO<sub>2</sub>eq. emissions.

Stichnothe et al., 2009 [106] conducted LCA of fuel ethanol derived from municipal and food waste. The authors considered integrated waste management system with aim of recycling and ethanol production from waste. Processing of one ton waste was the functional unit considered and results revealed that GHG emissions using integrated technology were 6.1gCO<sub>2</sub>eq.MJ<sup>-1</sup> where as gasoline GHG emissions were 87 gCO<sub>2</sub>eq.MJ<sup>-1</sup> and therefore savings of 92% GHG emissions were achieved.

Slade et al., 2009 [107] analyzed GHG emissions of cellulosic ethanol supply chains in Europe. Softwood and straw were modelled to produce ethanol using dilute acid (DA) and enzymatic hydrolysis (EH) process in Sweden and UK. GHG emissions from straw and softwood using DA and EH were 17, 32, 16 and 22 kgCO<sub>2</sub>eq.GJ<sup>-1</sup> ethanol respectively. The EH method although resulted in higher ethanol yield than DA but due to the use of enzymes contributed significantly to the emissions

Apart from sugarcane juice, bagasse is another most abundant feedstock for ethanol production in Brazil [108-111]. The sustainability of bagasse derived ethanol in Brazil has been studied by many authors [108, 112-114]. The conclusion derived from these studies is that GHG emission

reductions of 60-75% as compared to gasoline are achieved using bagasse derived ethanol.

Saga et al., 2010 [115] studied energy balance of ethanol produced from high yield variety of rice plant in Japan. Authors compared two scenarios, where in first scenario; cellulosic by-products such as husk and straw were used for cogeneration. In another scenario cellulosic material was diverted for ethanol production and left over residues such as lignin was used for electricity production. NEB of scenario 1 was 129.2 GJ/ha, which is far greater than NEB of scenario 1 (11.7 GJ/ha). The ethanol production in scenario 2 is just double than scenario 1, but at the same time energy input in conversion process of biomass to ethanol is 64% high and therefore, energy balance is lower than scenario 1.

Spatari et al., 2010 [77] conducted market price allocation between corn and stover and reported 65% lower emissions with respect to gasoline in near-term scenario. The corn based ethanol consumed large amount of energy during agriculture stage and consumption of natural gas in refining stage made the process emissions and energy intensive [99].

Kumar et al., 2011 [116] conducted well to pump LCA to study the environmental impact and net energy benefits of ethanol production using tall fescue grass straw as feedstock. Using different pretreatment processes GHG emissions were in the range of -0.013 to -0.055 kgCO<sub>2</sub>eq. MJ<sup>-1</sup> of ethanol and fossil energy required was in the range of -1507 to 3940 MJ. Among all pretreatment processes evaluated, steam explosion released minimum GHG emissions and least fossil energy use.

Wang et al., 2011 [117] evaluated well to wheel emissions for corn, sugarcane, switchgrass and miscanthus based ethanol in US. GHG emissions from corn stover were lowest (23gCO<sub>2</sub>eq.MJ<sup>-1</sup> ethanol) followed by switchgrass (23 gCO<sub>2</sub>eq.MJ<sup>-1</sup>ethanol), miscanthus (29 gCO<sub>2</sub>eq.MJ<sup>-1</sup> ethanol), sugarcane (45gCO<sub>2</sub>eq.MJ<sup>-1</sup>ethanol). Corn ethanol was worst in performance among all the feedstock with emissions of 76 gCO<sub>2</sub>eq.MJ<sup>-1</sup> ethanol. The corn ethanol performance is worst due to huge amount of fossil energy consumed in the agriculture phase and yield is also lower compared to other feedstocks.

Scown et al., 2012 [118] studied LCA of fuel ethanol derived from Miscanthus. The parameters having major impact on LCA results were emissions during agriculture phase and credits obtained while export of electricity to the grid. The GHG emissions were in the range of 11-13 gCO<sub>2</sub> eq.MJ<sup>-1</sup> corresponding to 80-90% lower emissions than gasoline.

Delivand et al., 2012 [119] while conducting environmental assessment of rice straw based ethanol showed net GHG emission release of 40.75 gCO<sub>2</sub>eq.MJ<sup>-1</sup> and production cost of 0.08 US\$/L.

Borrion et al., 2012 [120] assessed environmental sustainability of two ethanol blends E15 and E85 derived from wheat straw. The results were then compared with gasoline for travelling 1 km distance using similar car. The results showed that, life cycle GHG emissions for gasoline, E15 and E85 fuelled car were 330.09, 287.13 and 88.10 kgCO<sub>2</sub>eq. that corresponds to 13 and 73% reductions than gasoline.

Roy et al., 2012 [121] studied net energy consumption, CO<sub>2</sub> emission and production costs to determine whether environmentally preferable and economically viable ethanol can be produced from rice straw. The net energy consumption, CO<sub>2</sub> emission and production costs were estimated to be 10.0-17.6 MJ/L, -0.5-1.6 kg/L and 0.84-1.44.3 \$/L respectively, depending on the feedstock and scenarios of this study. Roy et al. also evaluated life cycle of bioethanol produced from rice straw by RT-CaCCO process. The study revealed that despite of environmental benefits, the economic viability of ethanol is doubtful unless innovative technologies including the renewable energy policy and stakeholders participation are considered.

In most of the 2G ethanol studies, lignin residue left after fermentation is used for electricity production. Apart from electricity use, Pourhashem et al., 2013 [122] studied three alternate use of lignin as: (1) soil organic carbon (SOC) enhancer (2) dried and sold to replace coal and electricity (3) used in biorefinery for on-site production of electricity. The authors noted that lowest are the emissions when the lignin is used as SOC enhancer (-25 to -2 g CO<sub>2</sub>eq. MJ<sup>-1</sup>) followed by use for electricity production (4-32 gCO<sub>2</sub>eq.MJ<sup>-1</sup>) and highest when utilized for onsite electricity production (36-41 gCO<sub>2</sub>eq.MJ<sup>-1</sup> ethanol).

Many authors have identified the use of enzymes in 2G ethanol production chain as the emission hotspot. Yan et al., 2013 [123] studied the GHG emission from enzyme use during ethanol production and reported to be 10.2-16.0 gCO<sub>2</sub>eq./g enzyme protein depending on the onsite Vs offsite production. The on-site and off-site production of enzymes contribute to emissions of 258 and 403 gCO<sub>2</sub>eq./L ethanol respectively. Due to avoidance of activities such as stabilizing and transportation of enzymes, GHG emissions are lower in on-site production.

Wang et al., 2013 [124] assessed environmental impact of ethanol production from wheat straw in UK using different pretreatment technology. The work concluded that steam explosion has lowest burden on environmental emissions among all pretreatments (dilute acid, ammonia and liquid hot water) due to lower requirement of process thermal energy and higher ethanol yield. Enzyme production was the main contributor to emissions as it requires a lot of fossil energy during its production. After excluding straw cultivation and harvesting, the ethanol production using SE pretreatment emitted 1.7 kg CO<sub>2</sub>/L ethanol. The ethanol production from wheat straw shows potential to replace gasoline by reducing 45-75% using different pretreatments. Similar results proving SE technology superior in terms of environmental and energy benefits were shown by the results of Kumar et al., 2012[125] and recently by Prasad et al., 2016 [126].

Kunimitsu et al., 2013 [127] studied LCA and LCC of straw ethanol in Vietnam. The authors studied 3 scenarios: (1) current technology using conc. H<sub>2</sub>SO<sub>4</sub>; (2) technological advances using conc. H<sub>2</sub>SO<sub>4</sub> with higher ethanol yield (3) innovative technology of wet disk milling. Overall it was found that current scenario has negative impact on both emissions and cost whereas using advanced technology only emissions can be lowered down and using innovation in process can bring both environment and economic benefits. The authors found that GHG emissions in 2 and 3 scenario can be reduced to 1454 and 1023 kg from 2135 kg in scenario 1.

Luk et al., 2013 [128] evaluated life cycle energy use and GHG emissions of lignocellulosic ethanol and electricity use in US light-duty vehicles. E85 and electricity pathways had similar life cycle fossil energy use

(~100 MJ/100 vehicle km traveled [VKT] and net GHG emissions (~5 kg CO<sub>2</sub>eq./100 VKT) that accounted considerably 65-85% lower emissions than gasoline and US grid electricity pathways.

Munoz et al., 2013 [129] assessed cradle to gate ethanol production from corn stover and grain in USA. The functional unit was production of 1 kg ethanol and results were compared to ethanol produced from fossil ethylene. Well to gate GHG emissions per FU ranged from 0.7-1.5 and 1.3-2 kg CO<sub>2</sub>eq. if use phase is also included. Fossil based ethanol emissions varied from 1.3-3.7 kgCO<sub>2</sub>eq.kg<sup>-1</sup> and thus ~50% reduction in emissions is achieved using bio based ethanol.

Murphy and Kendall, 2014 [130] analyzed life cycle of corn stover and switchgrass ethanol. The authors modeled wide range of scenarios by varying feedstock, conversion process and looking current and future possibilities. On an average GHG emissions of approx. 45-60 gCO<sub>2</sub>eq.MJ<sup>-1</sup> were emitted when co-products are not considered and 20-30 gCO<sub>2</sub>eq.MJ<sup>-1</sup> when byproducts are utilized to produce electricity. The agriculture practices, pretreatment and transportation activities were the emission hotspots in many of the scenarios.

Jansen et al., 2014 [131] studied influence of high gravity process conditions on environmental impacts of wheat straw based ethanol. The results showed that of experiments conducted at 20 and 30% solid loading using Cellic Ctech2 enzyme at 5 FPU/gm WIS showed GWP of 59.1 and 61.2 kg CO<sub>2</sub> eq. The study concluded that experiments using higher solid content leads to higher environmental burdens. However, impacts can be reduced by the addition of surfactants such as poly ethylene glycol (PEG) at higher solid loadings that can also give higher ethanol yield.

Karlsson et al., 2014 [86] conducted LCA of straw and forest residues based ethanol. GHG emissions and energy balance were analyzed using ISO and EU RED methodology. The results varied depending on inclusion/exclusion of agricultural activities, allocation method applied and calculation methodology used. The study concluded that important emission hotspots were process inputs in terms of enzymes and changes in soil organic carbon content due to removal of residues. Straw based ethanol generally gave

higher GHG emissions than produced from forest residues ethanol. The GHG savings for both feedstock with respect to gasoline were 51–84%.

Olukoya et al., 2014 [132] conducted LCA of ethanol from red cedar tree using bisulphite pretreatment followed by hydrolysis and fermentation. Cradle to gate LCA was conducted and results were compared to corn ethanol. The GHG emissions using 10, 15 and 20% NaHSO<sub>3</sub> resulted in 0.17, 0.18 and 0.21 kg CO<sub>2</sub> eq. emissions respectively. The study concluded that acid bisulfite pretreatment alone is responsible for 81% of fossil energy use, 65% GHG emissions and 77% of water use in overall process.

Pourbafrani et al., 2014 [133] studied impacts of pretreatment technologies and co-products on GHG emissions and energy use using alternative pretreatment technologies (DA hydrolysis, AFEX and AH) and co-products (electricity, pellet, protein and xylitol) for ethanol production from corn stover. Results showed that the choices of pre-treatment technology and co-product(s) impact ethanol yield, GHG emissions and life cycle energy use. DA exhibit 20-25% higher ethanol yields 15-25% lower net energy use than other pretreatment methods. The GHG emissions of E85 blend range from -38.5 to 37.2 gCO<sub>2</sub>eq.MJ<sup>-1</sup> and thus reducing emissions from 61% to 141% relative to gasoline.

Mandade et al., 2015 [134] conducted LCA of fuel ethanol from lignocellulosic biomass such as wheat stalk, sorghum stalk, rice husk, cotton stalk and sugarcane. The author evaluated the impact of ethanol production on energy, GHG emissions, land and water. These results were compared with molasses and sugarcane juice based ethanol, the conventional approaches for ethanol production in India. GHG emissions for cotton stalk, rice husk, wheat stalk, sorghum stalk, bagasse, molasses and sugarcane juice were 0.24, 0.45, 0.38, 0.16, 0.22, 0.16 and 0.53 kgCO<sub>2</sub>eq./L ethanol. The results of the analysis indicated that sorghum stalk is most favorable option due to its high NER, low GHG emissions and low land and water use. Ethanol from rice husk revealed relatively higher water usage and GHG emissions, but was within the margin of variability of other fuels.

Lever, 2015 [135] modeled the energy performance of wheat straw to ethanol production incorporating onsite production of cellulase and biogas to

meet energy requirements. The results showed that while doing such practices energy requirement reduced to 80–90 % and NER ranging from 6-9 is obtained.

In a review paper by Morales et al., 2015 [78] author studied LCA of more than 100 case studies published in past few years. The conclusion derived from these studies is that fuel ethanol resulted in lower GHG emissions and ozone layer depletion as compared to gasoline. However, in most studies eutrophication and acidification potential of ethanol was found to be negative. The LCA results are always dependent on the feedstock and blending volumes used in vehicles. GHG emissions can be reduced to ~10 and 85% using E10 and E85 blends. Most of the reviewed studies [82, 136-138] found that 2G ethanol production is environmentally and energetically sustainable, being the result are dependent on the possibility of utilizing c-products.

Orikiasa et al., 2015 [139] studied three different pretreatment methods for ethanol production. These include DiSC (direct saccharification of culms), RT-CaCCO (room temperature-CaCCO) and CaCCO (calcium capturing by carbonation) and reduction in GHG emissions as compared to gasoline were 59%, 42% and -3.5% and NER values were 2.7, 2.1 and 1.0 respectively. The total production cost estimated were 1.02, 1.34 and 151 \$/L ethanol in DiSC, RT-CaCCO and CaCCO respectively.

Rojas et al., 2015 [140] conducted environmental and economic LCA of bagasse derived ethanol in Brazil and identified enzyme use as energy and emission hotspots in the ethanol production chain. Petrsen et al., 2015 [141] and Agostino et. al., 2015 [142] identified enzyme production as the energy and emission hotspot during life cycle of ethanol. The authors said that approximately 24 kgCO<sub>2</sub>eq.emissions are released from 1kg of enzyme produced.

Sebastião et al., 2016 [143] conducted LCA of advanced ethanol from pulp and paper sludge. Two optimization scenarios were evaluated: (1) lowering dosage of acid during neutralization and (2) co-fermentation of C5 and C6 sugars. The results showed that co-fermentation scenario had 60

$\text{gCO}_2\text{eq.MJ}^{-1}$  emissions as compared to  $71 \text{ gCO}_2\text{eq.MJ}^{-1}$  in base case and  $55 \text{ gCO}_2\text{eq.MJ}^{-1}$  in scenario using reduced HCl.

Gilipin et al., 2016 [144] compared attributional LCA of 1 kg cellulase enzyme (CE) production on-site using submerged aerobic fermentation from glucose, sugarcane molasses and pretreated softwood as carbon source. CE production from pretreated softwood provided the lowest GHG emissions (7.9), followed by molasses (9.1) and cornstarch glucose (10.6)  $\text{kgCO}_2\text{eq.}$  respectively.

Zech et al., 2016 [145] conducted environmental and economic assessment of Inbicon lignocellulosic ethanol technology varying the feedstock, pentose-use, process energy, enzyme production and location parameters. In all scenarios the GHG emissions of ethanol production were 50% lower as compared to gasoline. Among all the scenarios, the ethanol production from co-fermentation of C5 sugars along with use of heat and steam generated internally from biogas released minimum GHG emissions of  $28.3 \text{ kg CO}_2\text{eq.MJ}^{-1}$  and cost of  $0.27 \text{ €}.\text{MJ}^{-1}$  ethanol.

Buck et al., 2016 [146] studied life cycle of from a mixture of hemp straw and triticale seeds and reported that ethanol can be produced for  $0.51\text{-}0.81 \text{ €}.\text{L}^{-1}$  ( $0.66 \text{ €}$  for current conditions) with  $\text{CO}_2$  abatement costs vary from  $38\text{-}262 \text{ € t}^{-1}.\text{CO}_2\text{eq.}$

Singh et al., 2016 [147] in a review paper discussed the environmental sustainability issues that can arise while producing 2G ethanol from rice straw at commercial scale in India. The authors revealed that although ethanol is considered as carbon neutral but the concerns about the emissions during collection, transportation, pretreatment, hydrolysis and distillation cannot be neglected.

The most surplus cellulosic feedstock available for ethanol production is rice straw in India [147, 148]. Soam et al., 2016 [149] compared dilute acid (DA) and steam explosion (SE) pretreatment for ethanol production from rice straw in India and reported GHG emissions to be reduced by 76 and 89% using DA and SE respectively. Authors further analyzed the NER of fuel ethanol which was found to be between 2.4-2.7.

Chang et al., 2017 [150] studied LCA of ethanol production from rice straw, napier grass and eucalyptus using different waste reutilization strategies.

### **2.3 LCA STUDIES OF RICE STRAW UTILIZATION PRACTICES**

Open burning of rice straw in fields is a major environmental problem in rice producing countries [151, 152]. Therefore, in order to avoid the burning, several authors studied different options to utilize the straw in form of electricity [153-155], ethanol [156], biogas [157-163], dimethyl ether (DME) [164] etc. Other uses include incorporation into the field [165-169] and use it as fertilizer [165-169] as an animal fodder [170] etc. Therefore, it is also essential to compare the performance of different utilization practices of rice straw from an environmental perspective.

Silialertruksa and Gheewala, 2013 [171] compared LCA of five different rice straw utilization practices such as for production of electricity, ethanol, biogas, DME and use as fertilizer. Processing of one ton rice straw was the FU. The results showed that, ethanol pathway resulted in the highest GHG emission reductions of 283 kg CO<sub>2</sub> eq. followed by DME (245 kg), electricity (116 kg) and fertilizer (67 kg). The straw based DME brought highest reduction of 0.3 kg SO<sub>2</sub> eq./ ton straw in acidification. In POCP, all four practices showed almost similar reductions of 0.8-1.0 kg C<sub>2</sub>H<sub>4</sub> eq./ ton straw.

Delivand et al., 2011 [172] studied environmental and economic benefits of utilizing rice straw in Thailand. The life cycle analysis results revealed that if straw based electricity replaces natural gas based electricity then 0.378 tCO<sub>2</sub>eq.t<sup>-1</sup> straw or 0.496 kgCO<sub>2</sub>eq.kWh<sup>-1</sup> emissions are avoided and if replaces coal based electricity then 0.683 tCO<sub>2</sub>eq.t<sup>-1</sup> straw (0.959 kg CO<sub>2</sub>eq/kWh) are avoided. Furthermore, straw use in power sector of Thailand could result in 7-9% reduction in import of crude oil.

Shafie et al., 2014 [153] conducted LCA of straw based electricity in Malaysia and compare GHG emissions with that of natural gas and coal. It

was found that for producing 1 kWh of electricity straw resulted in 0.36 kg CO<sub>2</sub> whereas coal and natural gas released 1.21 and 0.45 kg CO<sub>2</sub> emissions respectively. GHG emissions of about 1.05 kgCO<sub>2</sub>eq.kWh<sup>-1</sup> compared to coal-based power generation.

Gao et al., 2015 [172] together with energy evaluation created LCA model for four different rice straw utilization practices including ethanol, electricity, medium density fiberboard (MDF) and corrugated base paper (CBP). The results showed that ethanol was the most sustainable option of utilizing straw that resulted in GHG savings by 82% as compare to open burning.

Lecksiwilai et al., 2016 [173] NER and GHG assessment of DME derived from rice straw in Thailand. Compared to coal based DME emissions of 5.5 kgCO<sub>2</sub>eq.kg<sup>-1</sup> DME and NER of 0.58, rice straw based DME only produced 1.24 kgCO<sub>2</sub>eq.kg<sup>-1</sup> GHG and gave NER of 2.38. Similarly, Silialertruska et al. conducted LCA of using rice straw for DME production and compared used as automotive fuel for diesel engines and as LPG supplement for household application. The results revealed that bio- DME use as fuel and LPG can reduce GHG emissions by around 14–70% and 2–66% respectively.