Title Page

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Title: Life cycle assessment of energy and GHG emissions during ethanol production from grass straws using various pretreatment processes

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Abstract

Background, aim and scope The aim of this study was to perform a well-to-pump life cycle assessment (LCA) to investigate the overall net energy balance and environmental impact of bioethanol production using Tall Fescue grass straw as feedstock. The energy requirements and green house gas (GHG) emissions were compared to those of gasoline to explore the potential of bioethanol as sustainable fuel.

Methods The functional unit used in the study was 10000 MJ of energy. The data for grass seed production were collected from the farmers in Oregon and published reports. The compositions of straw, pretreatment and hydrolysis yields were obtained from laboratory experiments. Process models were developed for ethanol production using different pretreatment technologies in SuperPro Designer, to calculate the process energy, raw materials, utilities use and emissions related. The Greenhouse Gases Regulated Emissions and Energy use in Transportation (GREET) model and other literature studies were used to obtain additional data. Systematic boundary identification was performed using relative mass, energy, and economic value (RMEE) method using a 5% cutoff value.

Results and discussions Ethanol yields from grass straw were estimated 256.62, 255.8, 255.3 and 230.2 L/dry metric ton of biomass using dilute acid, dilute alkali, hot water and steam explosion pretreatments respectively. Fossil

energy required to produce one functional unit was in the range of -1507 to 3940 MJ for different ethanol production techniques. GHG emissions from ethanol LCA models were in the range of -131 to -555.4 kg CO_2 eq. per 10000 MJ of ethanol. Fossil energy use and GHG emissions during ethanol production were found to be lowest for steam explosion pretreatment among all pretreatment processes evaluated. Change in coproduct allocation from economic to mass basis during agricultural production resulted in 62.4% and 133.1% increase in fossil energy use and GHG emissions respectively.

Conclusions Technologies used for ethanol production process had major impact on the fossil energy use and GHG emissions. N_2O emissions from the nitrogen fertilizers were major contributor (77%) of total GHG emissions produced during agricultural activities. There was 57.43 to 112.67% reduction in fossil energy use to produce 10000 MJ of ethanol compared to gasoline, however about 0.35 hectare of land is also required to produce this energy.

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1. Introduction

Non-renewable fossil fuels account for about 88% of total energy used in 2008 (Brennan and Owende 2010). United States has the highest oil consumption (20.3 million barrels/day in 2005) in the world. Global climate change due to greenhouse gases (GHG) emissions from production and burning of fossil fuels is a major concern. Together with the increasing demand for energy sources, these concerns have led to alternative renewable energy sources. Transportation sector is one of the largest users of fossil fuels (da Costa Sousa et al. 2009). Ethanol is one of the promising alternatives of transportation fuels. Ethanol can be produced from fermentation of sugars, which can be obtained from starch rich feedstocks or lignocellulosic biomass. Presently, ethanol production from corn, wheat and sugar beet is the largest source of bioethanol. However capacity limitations and competition with food and feed sources (Bai et al. 2010) and intensive use of agricultural inputs among many other concerns necessitate research for other alternatives.

Lignocellulosic biomass (e.g., agricultural residues, grasses, forestry wastes, wastepaper, and various industrial wastes) are non food feedstocks that can be used to produce gases, solid or liquid biofuels. Their abundance and comparatively lower cost make them more attractive as a source of bioenergy (Teymouri et al. 2004; Sun and Cheng 2002). Liquid fuels produced from lignocellulosic biomass can result in less fossil energy use and low green house gas (GHG) emissions during their life cycle (Spatari et al. 2010; Spatari et al. 2005).

Lignocellulosic feedstocks contain 65 to 75% carbohydrates (35% to 50% cellulose and 20% to 35% hemicellulose) (Wyman 1996) and 10-30% lignin (da Costa Sousa et al. 2009). Carbohydrates can be hydrolyzed into sugar monomers (cellulose to glucose and hemicellulose to xylose, galactose, arabinose and mannose) using chemicals or enzymes and converted to ethanol/butanol or other value added compounds. Complex structure of cellulose, hemicellulose and lignin leads to biomass recalcitrance. Thus pretreatment process is an essential step in any biochemical conversion process to hydrolyze structural carbohydrates into sugar monomers. Additionally, lignin acts as a glue that binds cellulose and hemicellulose and acts as protective barrier to microorganisms (Kumar et al. 2009). Pretreatment process helps in enhancing the hydrolysis efficiency by removing the hemicellulose and lignin and altering the biomass structure (increase in porosity, surface area and decrease in crystallinity) (Kumar and Murthy 2011b; Kumar et al. 2009; Taherzadeh and Karimi 2007; Eggeman and Elander 2005; Sun and Cheng 2002). Different types of pretreatment processes have been developed and studied extensively for lignocellulosic

feedstocks: physical (e.g. mechanical comminution), chemical (e.g. dilute acid, dilute alkali, lime, hot water, ammonia percolation), physico-chemical (e.g. steam explosion, catalyzed steam explosion, Ammonia fiber expansion (AFEX)), and biological pretreatments (e.g. using white rot fungi) (Kazi et al. 2010; Kumar et al. 2009; Taherzadeh and Karimi 2007; Mosier et al. 2005b; Eggeman and Elander 2005; Sun and Cheng 2002). The pretreatment process is an important step in the ethanol conversion process that determines the ethanol yields, process energy and chemicals used in the process.

Grass straws, co-product of grass seed production, are potential feedstocks for ethanol production in Pacific Northwest US (Kumar and Murthy 2011b; Graf and Koehler 2002). At 330,823 Mg/year, Oregon is the largest producer of grass seed in the world (Oregon Seed Extension Program). About 0.88 million ton of grass straw is available every year in Oregon as a coproduct from grass seed production (Banowetz et al. 2008). Most of this production (~65% of total US production) is concentrated in the Willamette Valley, Oregon which is sometimes called 'The grass seed capital of world'. The common practice to manage the grass straw was to burn it in the fields, which have advantages like disease control, weed and insect control, nutrient recycling. However, new regulations have restricted burning of grass fields to avoid pollution in Oregon and Washington states (Steiner et al. 2006). More than 534,000 tons of grass straw is exported each year to Asian countries from western Oregon for use in animal feed rations (Steiner et al. 2006). Some amount of straw is also used in cardboard production in local market (Graf and Koehler 2002). Some varieties of grass seed produces a large amount of straw (up to 5 tons/acre) that contains high amount of cellulose (up to 31% w/w), and thus could potentially be used for ethanol production to meet regional needs.

Many Life cycle assessment (LCA) studies for ethanol have concluded that lignocellulosic ethanol causes less greenhouse gas (GHG) emissions and fossil energy use compared to petroleum fuels and corn-derived ethanol (Spatari et al. 2010; Bai et al. 2010; Luo et al. 2009a; Nguyen and Gheewala 2008; Spatari et al. 2005). Life cycle analysis, a useful technique to assess impact of products, processes and services on the environment, can play an important role in comparing ethanol fuel with other fuel alternatives based on environmental impact (fossil energy and GHG emissions). Most of the studies for LCA of ethanol are attributional LCA and very few consequential LCA have been reported to date. An attributional LCA can also be helpful in identifying the key areas in the whole fuel production cycle, by modifying which environmental impact can be reduced (Brander et al. 2009; Schmidt 2008). A complete “well to wheel” LCA is a variant of general LCA for transportation fuels with the system boundaries that

include: biomass production, transportation, ethanol production and fuel use. In last decade, due to increasing interest in global impact of fossil fuels and finding alternatives, many studies have been published on life cycle of ethanol production from lignocellulosic feedstocks (Spatari et al. 2010; Bai et al. 2010; Luo et al. 2009b; MacLean and Spatari 2009; Schmer et al. 2008; Nguyen and Gheewala 2008; Spatari et al. 2005). However, there are few ethanol LCA studies that have included detailed ethanol production process (MacLean and Spatari 2009).

Energy use during the conversion of cellulosic feedstocks into ethanol is highly dependent on the processing technologies. Optimum process conditions for maximum ethanol production depend on the type of lignocellulosic feedstocks (e.g. agricultural residues, softwoods, hardwoods, forest residues) and conversion technologies used. There is a great variability in technologies used for cellulosic ethanol production especially in pretreatment process, hydrolysis and fermentation techniques. This variability in addition to varying system boundaries is one of the main reasons for different results from ethanol life cycle studies. For example, Spatari et al. (2005) developed a life cycle of ethanol production from corn stover and switchgrass and use of ethanol high-level (E85-85% ethanol and 15% gasoline on volume basis) blends and concluded that as compared to reformulated gasoline, there was about 57% and 65% less GHG emissions (based on gram of carbon dioxide equivalent per kilometer) by using E85 from switchgrass and corn stover respectively. Schmer et al. (2008) estimated 94% lower GHG emissions from ethanol production from switchgrass than those of gasoline. Maclean and Spatari (2009) performed a "well to tank" life cycle of ethanol production from switchgrass using different ethanol production technologies. They observed that fossil energy use and GHG emissions were significantly less (65-70 %) for lignocellulosic ethanol than that of corn ethanol. Chemicals and enzymes used during ethanol production contributed for 30-40% of total fossil energy used. Bai et al. (2010) conducted life cycle analysis of ethanol production from switchgrass and concluded that GHG emissions from life cycle of ethanol to drive a midsize car for 1km (using E85) were about 65% less as compared to those of gasoline. Therefore there is a need for conducting LCA on a consistent basis with detailed process models that account for differences in pretreatment processes. We had demonstrated that different pretreatment processes can have significant differences in total and fossil energy use, water consumption, ethanol yields and capital costs (Kumar and Murthy 2011a).

The objective of this study was to evaluate the energy balance and GHG emissions from ethanol production from grass straw in Pacific Northwest US. Four ethanol production processes using different pretreatment processes: dilute acid, dilute alkali, hot water and steam explosion were analyzed using process simulations. The energy use

and emissions associated during whole life cycle of ethanol from grass straws were estimated and compared with those of gasoline, corn ethanol and other literature studies to evaluate the sustainability of grass straws as feedstocks for ethanol production.

2. Scope of study

The goal of this study is to provide information on life cycle emissions and energy use from ethanol production from grass straw. There are very few commercial scale plants producing cellulosic ethanol and there is a great variability in ethanol production technologies. This study analyzed the effect of different production techniques on the impact on environment using process modeling techniques. The functional unit for LCA analysis in this study is 10,000 MJ of energy from ethanol.

2.1 Data organization and specificity

The collected data for different processes such as chemicals productions, utilities (steam, electricity etc.) and transportation were organized in a Microsoft Excel spreadsheet. Most of the variable input data values were listed separately to increase the transparency and reusability of spreadsheet. Most of the data used in this study are specific to the USA. As the state of Oregon is major producer of grass straw, grass seed agricultural data (production yields, fertilizers and herbicides application rates, seed used, machinery use etc.) is specific to Oregon.

3. Methodology

3.1 Data for Life Cycle Inventory

The data for grass seed production were collected from the farmers in Oregon (Rose Agriseeds, Inc.), Enterprise budget (Oregon Agricultural Enterprise Budgets) and were verified with literature values. Most of the required data was collected from the GREET 1.8d model (The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET)). Published reports and research papers were also used to obtain some data particular to some region or technology. The data for ethanol production process: chemicals used; ethanol yields; co-products; energy use (steam, cooling water, electricity etc.) and emissions, were obtained from developed process models and can be found in Kumar and Murthy (2011a). All data sources used for this study are summarized in Table 1.

3.2 Assumptions

For all fuels (gasoline, diesel, ethanol), lower heating values (LHV) were used for energy calculations as LHV is more appropriate for energy calculation in vehicle applications than higher heating values (HHV) (Kim and Dale 2005; Bossel 2003). Major assumptions used in different processes in the ethanol LCA are summarized in Table 2.

3.3 System Boundary

The system boundary for analysis was selected using relative mass, energy, and economic value (RMEE) method (Raynolds et al. 2000) using a 5% cutoff value. In this method, mass, energy and economic value of each input are calculated starting from the unit process nearest to functional unit. Ratios of that input to functional unit are calculated in terms of mass, energy and economic value. If any of three ratios exceeds the predefined cut off ratio (5% in this work), upstream process of that input is included in the system boundary (Sander and Murthy 2010; Raynolds et al. 2000). This approach avoids the arbitrary elimination or selection of a unit process in the complete ethanol LCA. Functional unit, 10000 MJ of ethanol energy, is equivalent to 470.05 L (124.17 gal) or 371.03 kg of ethanol. Economic value of functional unit was estimated about $410 assuming ethanol price of $0.87/L ($3.3/gal).

3.4 Process Description

Complete well to pump analysis was divided into four main sections comprising biomass production, biomass transportation, ethanol production and ethanol distribution. The details of processes, assumptions and data inventory of each section are discussed below.

3.4.1 Biomass production

A large fraction of total energy used in life cycle of biomass based products is consumed in agricultural production activities (Kim et al. 2009). Tall Fescue (*Festuca arundinacea Schreb*) is one of the major grass straw producing crops in Pacific Northwest U.S, with average annual yield of 11.8 Mg/ha (Banowetz et al. 2008). However, all of the grass straw cannot be removed from the field. Some amount of the grass straw must be left on the field to reduce soil erosion and to maintain soil organic carbon content. It was assumed that 50% of the produced grass straw can be removed from the field without affecting the soil quality (White 2000). Straw from tall fescue (TF) contains about 31% cellulose, 20.2% hemicellulose and 14.4% lignin, with xylans constituting 82% of hemicellulose (Kumar and Murthy 2011b).

3.4.2 Biomass collection and transportation

Grass straw is transported in form of bales, which is most commonly used method for biomass transportation (Sokhansanj et al. 2010). The cost of baling the grass straw is $30-35 dollars per ton transported to a nearby site (Graf and Koehler 2002). Due to lack of data available on grass straw collection, fossil energy use and emissions based on diesel used during straw collection were assumed to be same as those reported for corn stover (313.7 MJ/Mg biomass fossil energy and 6.7 kg CO_2 eq./Mg emissions) (Sokhansanj et al. 2010).

Distance required to transport biomass depends on the scale of production plant and area required to collect required amount of biomass for ethanol production plant. Area required to collect required amount of grass straw was calculated using equation 1.

$$Area_{collect} = \frac{D_{straw}}{Y_{straw} * F_{cropland} * F_{avail} * F_{collect}} \quad (1)$$

Where, D_{straw} = Annual demand of straw for ethanol plant; Y_{straw} = Annual yield of straw per unit area; $F_{cropland}$ = Fraction of area under fields (some area is covered by roads, homes and other buildings); F_{avail} = Fraction of farm land which grows grass straw; $F_{collect}$ = Fraction of straw that can be removed from fields without affecting the soil quality.

The values of $F_{cropland}$, F_{avail} and $F_{collect}$ were assumed 0.6, 0.75 and 0.5 respectively. Assuming the plant to be located in the center of grass seed farmland, distance required (radius of circle) to supply the required amount of straw (250,000 metric ton biomass/ year) for the plant was calculated as 17.25 km. Trucks were considered to be going empty one way. So, a total distance of 34.5km was considered for calculations of energy and emission from transportation.

3.4.3 Ethanol production

Efficiency of ethanol production process is highly dependent on the processing technologies used. For this study, four ethanol production processes using different pretreatment processes: dilute acid, dilute alkali, hot water and steam explosion were developed using Super Pro Designer (Intelligen, Inc., Scotch Plains, NJ) for a plant with processing capacity of 250,000 metric ton biomass/ year. A generic cellulosic ethanol production process is shown in Fig. 1. Biomass preparation includes the washing (removal of dirt and stones) and size reduction of biomass to facilitate handling and process efficiencies. For production of ethanol, carbohydrates (sugar polymers) of biomass are hydrolyzed to monomers using chemicals or enzymes. Pretreatment is performed before the hydrolysis process

to remove hemicellulose and lignin and to open the structure of biomass. The sugars obtained from hydrolysis are fermented to alcohol. Ethanol is recovered from the fermented broth using combinations of distillation and molecular sieves. Residual cellulose and hemicellulose along with lignin are used for steam and electricity production by combustion in a fluidized bed reactor (Kazi et al. 2010; Laser et al. 2009; Aden et al. 2002).

The four pretreatment methods analyzed in this study are most commonly used methods for biomass pretreatment and have been studied thoroughly by many researchers for various feedstocks (Kumar and Murthy 2011b; Xu 2011; Hu and Wen 2008; Chen et al. 2007; Linde et al. 2007; Ballesteros et al. 2006; Hamelinck et al. 2005; Mosier et al. 2005a; Lloyd and Wyman 2005; Wyman et al. 2005; Sun and Cheng 2005; Aden et al. 2002). Process conditions, efficiencies, advantages and limitations of these pretreatment processes have been discussed in many review papers (da Costa Sousa et al. 2009; Kumar et al. 2009; Taherzadeh and Karimi 2007; Mosier et al. 2005b; Sun and Cheng 2002). All pretreatment models in the present study were modeled for 20% solid loading, except for steam explosion, which was simulated at 30% solid loading. All pretreatments except steam explosion were simulated at 180°C operating temperature and 15 min residence time. Residence time of 5 min was used for steam explosion model. Acid/alkali concentrations used for dilute acid and dilute alkali models were 1% on weight basis. Most of the hemicellulose is converted to its sugar monomers during pretreatment processes except for dilute alkali process. Significant amount of cellulose is also converted to glucose (~13%) during dilute acid pretreatment compared to other pretreatment processes (0.4%, 0.3% and 5% for hot water, dilute alkali and steam explosion pretreatment respectively). In case of dilute acid pretreatment, detoxification is performed after pretreatment by overliming process (Spatari et al. 2010; Aden et al. 2002). Simultaneous saccharification and fermentation (SSCoF) is the next step after pretreatment. Simultaneous saccharification and fermentation (SSCoF) process includes hydrolysis of cellulose and hemicellulose and simultaneous fermentation of hexose and pentose sugars (Spatari et al. 2010). The pretreated grass straw is hydrolyzed using commercial enzymes (blend of cellulases and hemicellulases) at an enzyme loading of 15 FPU/g of cellulose. Enzymatic hydrolysis efficiencies of cellulose for dilute acid, dilute alkali and hot water pretreated grass straw (79%, 84.75% and 78.5% respectively) were obtained from laboratory studies (Kumar and Murthy 2011b). Cellulose hydrolysis efficiency for steam explosion model was assumed as 70% (Kumar et al. 2009; Ballesteros et al. 2006). Hemicellulose hydrolysis efficiency was assumed as 80% in all models. The fermentation efficiencies of glucose and xylose were assumed to be 95% and 70% respectively. Ethanol from the fermented slurry is subsequently recovered using a distillation columns (beer column followed by rectification

column) and molecular sieves. The distillation design was based on NREL 2002 report (Aden et al. 2002). The bottom effluent of beer column is separated into solid stream (containing most of the lignin) and a liquid stream (containing most of the water and soluble solids). The lignin rich stream is combusted in fluidized bed combustor for steam generation. A fraction of liquid stream (25%) is treated in waste water treatment plant (series of anaerobic and aerobic digestions) and remaining stream is concentrated in multiple-effect evaporator. The condensate from the evaporator is recycled back as process water and concentrated syrup is fed to waste water treatment. Detailed chemical oxygen demand calculations were used to determine the biogas produced in anaerobic digestion of waste water (Barta et al. 2010). Biogas produced from waste water treatment is also burnt in combustor along with lignin stream. Steam produced from the fluidized bed combustor is primarily used to provide process heat required in the plant. Any excess steam is used to generate electricity. The details of these models and energy calculations are provided elsewhere (Kumar and Murthy 2011a).

3.4.4 Ethanol distribution

Ethanol is distributed from plant to bulk terminals from where it is transported to gas stations. Transportation from plants to bulk terminal occurs by barrage, train and trucks, whereas from terminal to gas stations, ethanol is transported mainly by diesel trucks. Default values of GREET model were used for ethanol distribution (40% by barrage, 40% by rail and 20% by trucks). Distribution distances of 520, 800 and 80 miles were assumed for ethanol distributed by barrage, train and trucks respectively. Transportation of ethanol from bulk terminals to pumps was assumed to occur by only trucks and a 30 mile distance was assumed for this study.

3.5 Co-product Allocation

During any fuel production, multiple products are formed, for example DDGS in corn ethanol and lignin in cellulosic ethanol. There are two multi product processes in the system: grass straw and grass seed production; ethanol and electricity production. Grass straw is not a main crop but a coproduct of grass seed production. There are different approaches to allocate energy and emissions during agriculture production: mass basis, economy basis or energy basis. System expansion approach described in detail by Kim and Dale (2002) is another approach that has been used in LCA studies. However that approach cannot be used for grass straw as grass straw is a co-product and produced grass seed is the main product and does not replace any other product. The allocation of energy and emissions during agricultural production of grass seed were done on economic basis.

Steam and electricity produced from lignin residues and biogas during ethanol production are other co-products in the system. The steam and electricity generated can be used to supply process steam and electricity required for the plant operations. Excess electricity produced can be sold to grid (Kazi et al. 2010; Spatari et al. 2010; Laser et al. 2009; Aden et al. 2002), therefore system expansion method (Kim and Dale 2002) was used to account for the electricity. It was assumed that this steam and electricity will replace the energy and emissions associated with required steam and electricity production from fossil energy sources.

4. Results and Discussion

The system showing all inputs included in the LCA study of ethanol is presented in Fig. 2. Some inputs such as diammonium phosphate (DAP), diesel used during transportation, coal, natural gas and petroleum used during ethanol distribution were outside the 5% RMEE boundary, however were included in the LCA system boundary.

4.1 Life Cycle Energy Use

Ethanol yields from TF grass straw were estimated as 256.62, 255.8, 255.3 and 230.2 L/dry metric ton of biomass from ethanol plants using dilute acid, dilute alkali, hot water and steam explosion pretreatments respectively. Ethanol yield is low for steam explosion pretreatment because of the assumption of low cellulose hydrolysis yield (70%) in the process model. Energy used during ethanol production process was calculated as the difference between the total energy input and co-product energy. As discussed earlier, co-products in this case are steam and electricity energy from lignin residues and biogas produced from waste water treatment. Fossil energy used for production of functional unit energy (10000 MJ of ethanol energy) during various stages of life cycle of ethanol using different ethanol production techniques have been illustrated in Fig. 3. For all pretreatment processes, co-product energy produced enough steam to exceed the process steam requirements in ethanol production process. However except for steam explosion process, use of all other pretreatment processes required grid electricity. In case of steam explosion pretreatment availability of excess electricity to export to grid after meeting the ethanol production process needs resulted in fossil energy credits. . Therefore, in Fig. 3 fossil energy use during ethanol production for steam explosion pretreatment is shown as large negative number while it is a positive number for all other pretreatment processes.

Ethanol production process had major contribution in the total fossil energy use in all models. Net fossil energy use was found negative for ethanol production in LCA using steam explosion pretreatment process. The reason for

negative fossil energy was low process energy used (thermal and electricity) and high co-product energy produced during ethanol production process. Energy from the co-products were more than process energy, so negative values of fossil energy is due to energy replaced by excess electricity, which was otherwise produced from fossil fuels. Ethanol yields, energy used, co-product energy produced during ethanol production processes for all pretreatment methods are presented in Table 3.

Fossil energy used was found maximum for ethanol produced using dilute alkali pretreatment. The values are higher than those of other models because of large fossil energy input for alkali production (16 MJ/kg sodium hydroxide). Fossil energy used during nitrogen fertilizers and herbicides production accounted for about 80% of total fossil energy used during grass straw production (Fig. 4a).

Net energy value (NEV), defined as the difference between energy in fuel and amount of fossil energy used in the production of fuel, is a key indicator of the fossil fuel displacement value of any biofuel (Eqn. 2). Net energy ratio (NER) and net fossil energy value (NFEV), other common terms used in LCA studies, were calculated using Eqns. 3 and 4 respectively.

$$\text{Net Energy Value} = \text{Energy in functional unit} - \text{fossil energy use to produce functional unit} \quad (2)$$

$$\text{Net energy ratio} = \frac{\text{Energy in functional unit}}{\text{Fossil Energy input}} \quad (3)$$

$$\text{Net fossil energy value} = \frac{\text{Energy in functional unit - Fossil Energy input}}{\text{Energy in functional unit}} \quad (4)$$

The fossil energy input mentioned in Eqns. 3 - 4 is net fossil energy required for production of functional unit after accounting for the co-product energy. Higher values of NEV and NER, indicate higher energy efficiency. Negative value of NEV or NER value less than 1.0 indicate that fossil energy used to produce fuel was more than that of energy content of fuel. Net energy value for ethanol was in the range of 4935.28 to 11507.8 MJ/ 10000 MJ (10.5 to 24.48 MJ/L ethanol) (Table 4). These values are comparable to NEV values estimated by Schmer et al. (2008) for ethanol production from switchgrass (more than 14.5 MJ/L ethanol). NEV values are positive for all models because of co-product energy. Lignin and biogas energy replaced the fossil energies required to produce process steam and electricity in production plant. The value of NFEV was negative for gasoline indicating that fossil energy input is higher than energy in the fuel (Table 4).

339 It should be noted that a fuel choice cannot be made solely on basis of NEV or NER as all fuels are not of equal
340 energy quality, e.g. one MJ of coal is not equal to 1 MJ of electricity in terms of its utility (Dale 2007). Such
341 comparisons are meaningful only for fuels of similar energy quality. Both ethanol and gasoline are transportation
342 fuels and can be considered to be of same quality, so net energy can be used as comparison basis. However, other
343 factors such as GHG emissions changes, total and fossil energy use are more informative for comparisons among
344 different fuels.

345 Total energy and fossil energy used to produce functional unit energy of ethanol, gasoline (GREET default) and
346 corn ethanol (GREET default) are presented in Fig. 5. Total energy values include energy in the functional unit
347 (10000 MJ). Fossil energy use for production of functional unit were found 66.88, 57.43, 68.14 and 112.67% less
348 than that for gasoline for ethanol produced using dilute acid, dilute alkali, hot water and steam explosion process
349 respectively.

350 4.2 Environmental Emissions

351 The GHG during different stages of life cycle of ethanol were calculated in terms of gram CO_2 equivalent using
352 global warming potential factors of 1, 25 and 298 for CO_2, CH_4 and N_2O respectively (GREET 1.8d). GHG
353 emissions from production of functional unit energy (10000 MJ) during various steps in ethanol production are
354 presented in Fig. 6. During ethanol production process, fossil energy use was found negative for steam explosion
355 process due to relatively high availability of electricity in case of steam explosion process (Fig. 3). The GHG
356 emissions can result from not only the production of utilities such as steam and electricity but also due to use of
357 chemicals. Therefore in Fig. 6, there is a small positive GHG emissions related to ethanol production (associated
358 primarily with the use of DAP during SSCoF process) while this number is much larger for other pretreatments. The
359 CO_2 released during ethanol fermentation and lignin burning was sequestered from environment by photosynthesis
360 process during grass straw production. Hence, CO_2 emissions produced during fermentation process and lignin
361 residue burning were not accounted into calculations. The results were presented on well to pump basis, so CO_2
362 sequestration that accounted for carbon in ethanol was subtracted from the total LCA emissions (Wang 2005;
363 Spatari et al. 2005). The GHG emissions from ethanol LCA models were estimated -255.6, -131.0, -237.7 and -
364 555.4 kg CO_2 eq. per functional unit (-501.2, -278.7, -505.7 and -1,181.6 g CO_2 eq./L ethanol) for ethanol
365 production processes using dilute acid, dilute alkali, hot water and steam explosion process respectively. The GHG

366 emissions in present study are higher than those reported by Spatari et al. (2005) for well to tank life cycle analysis
367 of ethanol from switchgrass and corn stover (-1,020 and -1,179 g CO_2 eq./L ethanol produced from switchgrass and
368 corn stover). These differences may be due to different assumptions assumed during ethanol production process
369 which resulted in higher ethanol yields (330-340 L/dry metric ton biomass vs. 230-257 L/dry metric ton biomass in
370 present study) and different process energies used.

371 Except for ethanol produced using steam explosion pretreatment, ethanol production process is major contributor of
372 GHG emissions. There is great variation on the energy use and emissions data on cellulase enzymes production
373 depending upon enzyme family and techniques used (Spatari et al. 2010). Maclean and Spatari (2009) mention a
374 possible range of 1000-10,000 g CO_2 eq./kg enzyme emissions depending upon the technology used. A value of
375 2,264 g CO_2 eq./kg enzyme was assumed for current study (MacLean and Spatari 2009). Emissions from enzyme
376 production in current study were in the range of 278.3 to 340 kg CO_2 eq./ 10000 MJ of ethanol produced, which are
377 higher than the values reported by Maclean and Spatari (2009) for LCA of switchgrass (less than 40 kg CO_2 eq./
378 10000 MJ of ethanol produced). The emissions were higher for present study because of relatively low enzyme
379 activity assumed (60 FPU/g enzymes vs. 485 FPU/g enzymes), which resulted in higher amounts of enzymes used
380 (62.4 – 71.8 g enzyme/kg biomass vs. 9-10 g enzyme/kg biomass). The enzyme activity assumption was based on
381 our laboratory measurement of commercial enzymes currently available (not reported). Enzyme usage has been
382 found different among various literature studies because of different enzyme activities assumed. The GHG
383 emissions were relatively much lower in case of steam explosion because of low thermal energy used and high co-
384 product energy during ethanol production process (Table 3). Energy use was relatively less in case of steam
385 explosion because of the assumption of high solid loading (30%), which decreases the process flow rates in the
386 plant. Electricity produced after supplying the process steam, was estimated to be in excess of the plant electricity
387 requirement and GHG emissions displaced by extra electricity produced from lignin residue were about 307 kg CO_2
388 eq. per functional unit.

389 During life cycle of ethanol, agricultural production activities are also major contributors to total GHG emissions
390 due to emissions of nitrous oxide (N_2O) in addition to CO_2. Although N_2O emissions are relatively less in quantity,
391 global warming potential of N_2O is much higher than that of CO_2 (298 for N_2O vs. 1 for CO_2) (GREET 1.8d).
392 Application of nitrogen fertilizers result in the N_2O emissions from soil due to microbial nitrification and
393 denitrification (direct) and nitrogen fertilizer leaching to groundwater as nitrate (Wu et al. 2006; Spatari et al. 2005).

Total N_2O emissions from soil were assumed as 1.5% of nitrogen in fertilizers applied. These N_2O emissions contributed significantly (77% in terms of CO_2 eq. basis) to the emissions during agricultural production process. The global warming factor for N_2O is 298 times that of CO_2 (Fig. 4b). It can be observed from Fig. 4a and 4b that fossil energy use does not correlate directly with GHG emissions. Volatile organic compounds (VOC), particulate matter (PM), sulfur oxides (SOx) etc. are some air pollutants produced during life cycle of ethanol. Although these pollutants are not considered as GHG emissions, they impact the environment. Estimated values of these pollutants along with GHG emissions during well to pump life cycle analysis of ethanol production of grass straw are presented in Table 5.

4.3 Well to wheel analysis

Well to wheel analysis also accounts for energy use and emissions during vehicle operation (Wang 2005). Ethanol is normally blended with gasoline as low blend (10-15%) or high blend (up to 85%). A Well to wheel analysis was performed for ethanol produced using dilute acid pretreatment process. Other than pure ethanol, two blends were considered in the study – E10 (10% ethanol and 90% gasoline) and E85 (85% ethanol and 15% gasoline). The fuel efficiency of midsized car (km/L fuel) was assumed as 0.32 km/MJ of fuel (gasoline, ethanol and ethanol blends) (Sheehan et al. 2003). The fossil energy required and GHG emissions per km of driving for gasoline, ethanol and ethanol blends are shown in Fig. 7 and 8 respectively. Fossil energy use and GHG emissions produced during life cycle of E85 to drive 1 km were about 53 and 39.12% less than those of gasoline respectively. Wang (2005) estimated 42.5 and 20.5% fossil energy reduction per kilometer (69.1 and 32.9% per mile) by using E85 blends of cellulosic and corn ethanol instead of gasoline. GHG emissions were observed to be reduced by 39.77% per kilometer (64% per mile) by using cellulosic ethanol E85 instead of gasoline respectively.

Ethanol fuel produced either from cellulosic biomass or corn ethanol is a better alternative to gasoline on basis of fossil energy use and GHG emissions. However the agricultural production of plant based feedstocks also requires use of land and water which are limited resources. In present study, it was estimated that about 0.35 hectare of land is required to produce functional unit energy. It was estimated that there was a 173 to 410% reductions in GHG emissions from production of functional unit of ethanol (10000 MJ) using different techniques compared to gasoline. However, 0.35 ha of land/functional unit is the additional resource that is required to achieve the reduced emissions.

Some life cycle studies on biofuels have discussed a concern on land use change due to production of biomass required for biofuels. However, grass straw is an agricultural residue and not a main crop. We have done analysis on the basis of already available biomass. Even the size of ethanol plant in models was decided on basis of current availability of biomass and did not consider expanding the agricultural land for extra grass seed production. So, land use change was not accounted in current study.

4.4 Sensitivity Analysis

As discussed earlier in the manuscript, other than economic basis, mass and energy values of products are common methods used for allocation of energy use and emissions to co-products produced. A sensitivity analysis was performed by changing the allocation method between grass seed and grass straw from economic basis to mass basis for dilute acid pretreatment model. As grass seed does not have significant lipid content, proximate composition of grass seed and straw were assumed to be similar. Therefore it was assumed that energy based allocation will give similar results as mass based allocation. On mass basis, production of grass straw is about 6.3 times than that of grass seed from unit agricultural land, whereas economic value of grass straw is only about 0.35 times that of grass seed. As the biomass/main crop allocation ratio is higher, more emissions and energy will be associated with biomass production, which will ultimately add to ethanol. On mass basis, grass straw shares about 75.7% of fossil energy used and GHG emissions produced during agricultural production activities, which was much higher than that on economic value basis (15%). The fossil energy used and GHG emissions from life cycle analysis increase by 62.4% and 133.1% respectively. GHG emissions were estimated to be about 78.078 kg CO_2 eq. per functional unit of ethanol (56% less than that of gasoline). Luo et al. (2009b) made similar observations when they changed the allocation basis from economic to mass/energy basis. They found that there was shift of 1.7 to 7.5 in corn/stover allocation ratio when allocations were based on economic value instead of mass/energy, which changed the entire results of LCA study. Conversion efficiency of biomass energy to electricity is a major factor that can affect the results of LCA study. Most of the literature models on ethanol production from cellulosic biomass reported net export of electricity produced from lignin residues from plant, which can displace the fossil energy and emissions from electricity production from fossil fuels. In the current study, electricity produced from lignin was estimated to be less than the ethanol plant electricity needs in all models except for steam explosion pretreatment. Biomass energy to electricity conversion efficiency was assumed as 30%. A sensitivity analysis was performed for ethanol LCA using dilute acid pretreatment for the range of biomass to electricity efficiencies (25 to 40%) reported in

449 literature. A change of -36.8 % and +18.5% GHG emissions were observed as the biomass to electricity efficiencies
450 were changed from 30% (base case) to 40 and 25% respectively. Fossil energy use and other parameters did not
451 change for these scenarios.

452 **5. Conclusions**

453 A "well to pump" life cycle analysis was conducted for ethanol production from tall fescue grass straw considering
454 four different pretreatment methods for ethanol production. Ethanol production process was found to be a major
455 contributor in the fossil energy used and GHG emissions produced during life cycle of ethanol. Depending on the
456 pretreatment process, there was 57.43 to 112.67% reduction in fossil energy required to produce functional unit in
457 ethanol life cycle analysis as compared to that of gasoline. Steam explosion process at high solid loading (30%)
458 resulted in net negative fossil energy use due to low thermal energy use and net export of electricity (co-product)
459 from the plant. Net energy value for ethanol was in the range of 10.5 to 24.48 MJ/L ethanol. The GHG emissions
460 from ethanol LCA models were in the range of -131 to -555.4 kg CO_2 eq. per 10000 MJ of ethanol. N_2O emissions
461 from the production and use of nitrogen fertilizers accounted for about 77% of total GHG emissions produced from
462 agricultural activities. Fossil energy use and GHG emissions produced from life cycle of E85 fuel required to drive 1
463 km were about 53 and 39.12% less than those of gasoline fuel. Changing the allocation method from economic to
464 mass basis for grass straw and grass seed resulted in 62.4% and 133.1% increase in fossil energy use and GHG
465 emissions.

466 **Acknowledgements**

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585

586 **Tables**

587 **Table 1** Summary of data sources

Unit Process	Data Source	Data gathered from source
Agriculture Production	Banowetz et al. (2008)	Straw yield, straw production in Pacific Northwest US
	Oregon Agricultural Enterprise Budgets, Rose Agriseeds, Inc.	Fertilizers, herbicide application rates, seed application rates, agricultural machinery (diesel) used
	GREET 1.8d	Energy use and emissions from fertilizers, herbicides, diesel production
Biomass Collection and Transportation	Sokhansanj et al. (2010)	Energy and emissions from straw collection
	GREET 1.8d	Fuel economy of trucks, emissions and energy use for transporting biomass
Ethanol Production	Kumar and Murthy (2011a)	Chemicals used, ethanol yield, energy use (steam, electricity etc), co-product energy
	Kumar and Murthy (2011b)	Pretreatment conditions, pretreatment efficiencies, cellulose hydrolysis efficiencies
	Maclean and Spatari (2009)	Energy use and emissions from cellulase enzymes and chemicals (NaOH and Di-ammonium phosphate (DAP)) production
	GREET 1.8d	Energy use and emissions from chemicals production (ex. H_2SO_4 and CaO)
Ethanol distribution	GREET 1.8d	Energy use and emissions from distribution of ethanol from plant to pumps by different transportation modes
Gasoline and corn ethanol life cycle	GREET 1.8d	Energy and emissions during life cycle of conventional gasoline and ethanol produced from corn grains
General	GREET 1.8d	Fuel densities, heating values

588

589 **Table 2** Summary of assumptions

Process	Assumptions
Agriculture Production	- Stand life for tall fescue was assumed as 3 years (1 year establishment and 2 year production)
	- 50% of straw is left in the field to maintain soil quality
	-N_2O emissions from soil were assumed same as those by switchgrass (1.5% of nitrogen in fertilizers applied) (Wu et al. 2006; Spatari et al. 2010)
Biomass Collection	- Energy and emissions from straw collection were assumed same as for corn stover as

and Transportation	calculated by Sokhansanj et al. (2010) - Biomass is transported in form of bales in heavy duty trucks
Ethanol Production	- Enzymes are purchased from commercial sources at a protein concentration of 10% and 60 FPU/g of enzyme broth (Kazi et al. 2010) - Thermal efficiency for boiler for steam generation from lignin residue was 75% (Prasad 1995; Mani et al. 2010) - Conversion efficiency of biomass energy to electricity was 30%
Ethanol distribution	- Default values of GREET model were used for ethanol distribution (percentage of ethanol distributed by different transportation modes and distance travelled from ethanol plant to bulk terminal through different modes) - Distance traveled from bulk terminal to pumps is 46 Km (30 miles)

590

591 **Table 3** Results of ethanol production models using different pretreatment processes*

	Dilute Acid	Dilute Alkali	Hot Water	Steam Explosion
Ethanol Yield (L/dry ton biomass)	256.65	255.83	255.30	230.25
Thermal Energy Use (MJ)	8935.31	8807.22	9087.42	6349.34
Electricity Use (kWh)	433.61	415.21	439.22	408.85
Water Use (kg)	2801.55	2850.33	2746.31	2050.26
Co-Product Energy** (MJ)	13270.54	13145.58	13696.10	16366.41
Electricity Produced (kWh)	361.25	361.51	384.04	834.71

592 * All results are per functional unit unless mentioned

593 ** Energy from lignin residue and biogas

594

595 **Table 4** Net energy value and net energy ratio for life cycle of ethanol

	Dilute Acid	Dilute Alkali	Hot Water	Steam Explosion	Gasoline
Net Energy Value (MJ/ 10000 MJ)	6059.65	4935.28	6209.62	11507.82	-1869.09
Net Energy Value (MJ/ L EtOH)	12.89	10.50	13.21	24.48	-
Net Energy Ratio	2.54	1.97	2.64	-	0.84
Net Fossil Energy Value	0.606	0.494	0.621	1.151	-0.190

596

597

598

599 **Table 5** Energy used and GHG emissions from well to pump LCA of ethanol production from grass straw*

	Dilute Acid	Dilute Alkali	Hot Water	Steam Explosion
Total Energy (MJ)	14548.95	15615.45	14371.38	9035.94
Fossil Energy (MJ)	3940.35	5064.72	3790.38	-1507.82
Emissions (g)				
CO_2 (kg)	-280.90	-174.64	-281.41	-590.83
CO	116.56	96.383	95.062	15.42
CH4	201.81	137.145	137.267	-318.29
N_2O	135.08	134.919	135.188	145.59
NOx	352.57	265.441	255.080	-79.69
VOC	69.65	63.577	63.235	39.16
PM10	123.31	76.914	77.274	-357.77
PM2.5	44.97	29.421	29.125	-84.90
Sox	355.64	270.330	268.500	-467.85
Total GHG Emissions (kg equivalent CO_2)	-235.60	-131.00	-237.70	-555.40

600 * All results are per functional unit unless mentioned

601 **List of Figures**

602 **Fig. 1** Generic process of ethanol production from lignocellulosic biomass

603 **Fig. 2** Process flow diagram of ethanol production from grass straw

604 **Fig.3** Fossil energy use per functional unit (10000 MJ ethanol energy) during various stages of life cycle of ethanol

605 **Fig.4** Fossil energy used and GHG emissions contribution from different inputs during grass straw production (a)
606 Fossil energy used (b) GHG emissions

607 **Fig.5** Total energy and fossil energy used for production of 10000 MJ of energy (1 functional unit) during life cycle
608 of cellulosic ethanol, gasoline and corn ethanol

609 **Fig.6** GHG emissions produced per functional unit (10000 MJ ethanol energy) during various stages of life cycle of
610 ethanol

611 **Fig.7** Total energy and fossil energy used from life cycles of different fuel blends required for one km driving

612 **Fig.8** GHG emissions produced from life cycles of different fuel blends required for one km driving

613

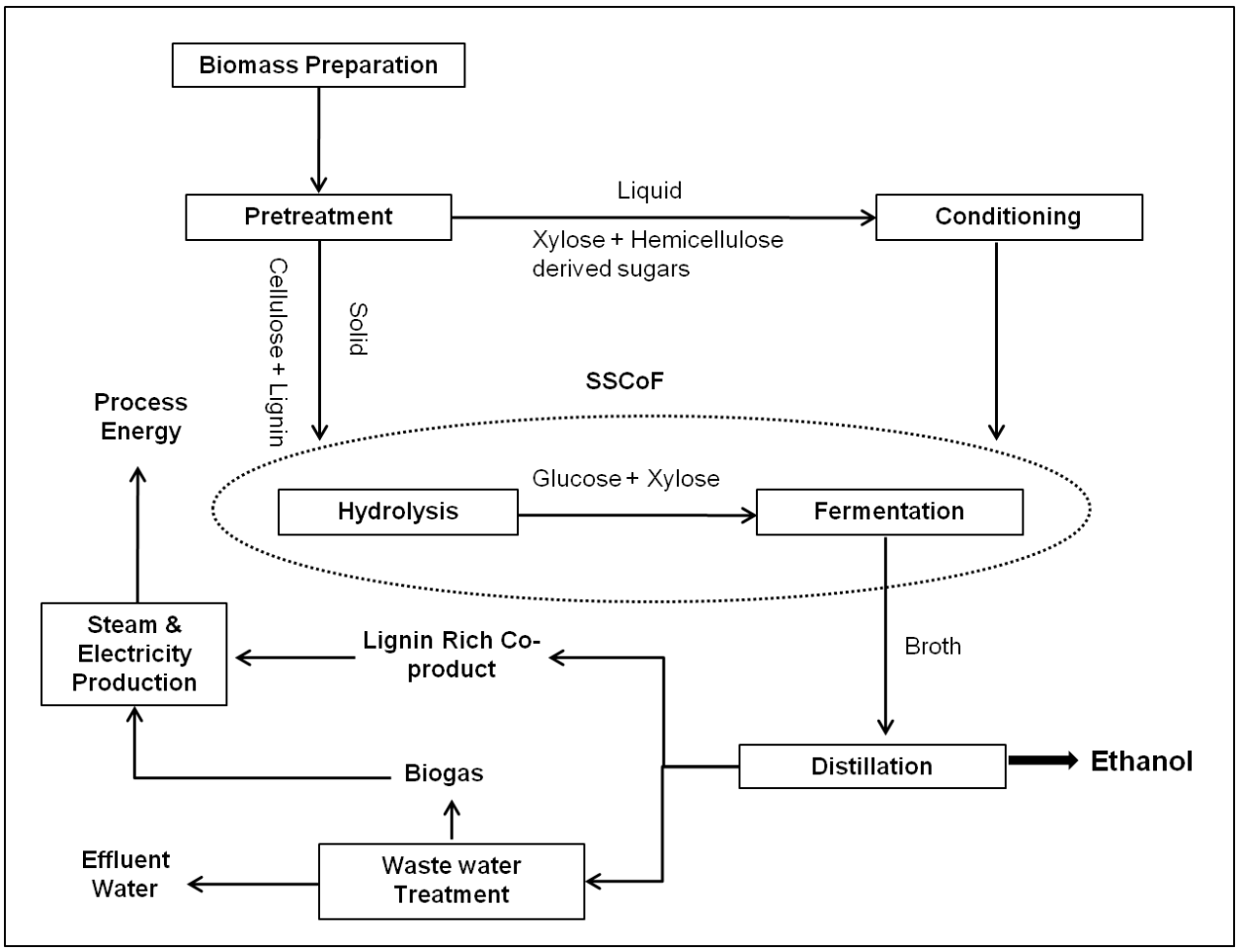
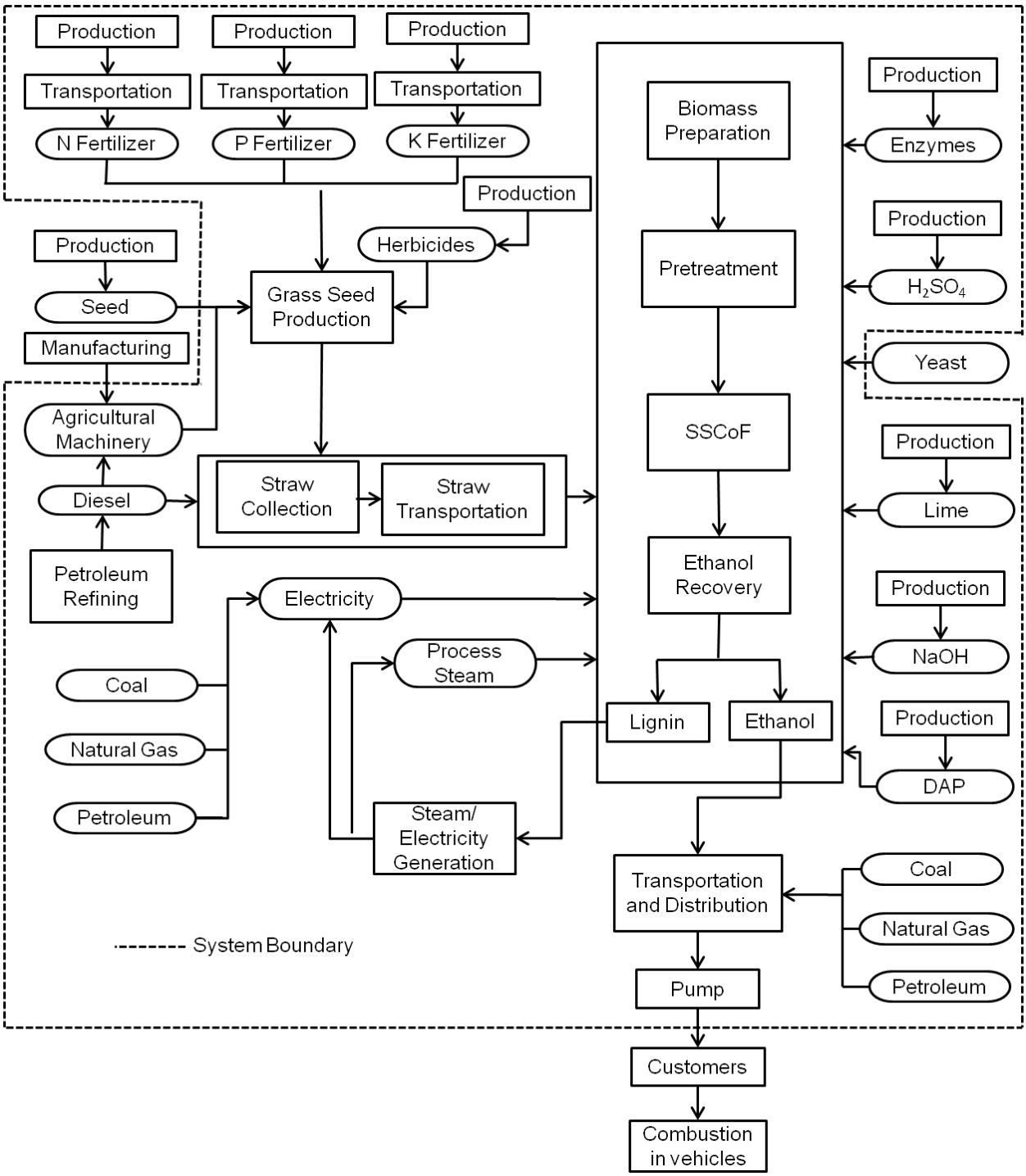


Figure 1 Generic process of ethanol production from lignocellulosic biomass



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618 **Figure 2** Process flow diagram of ethanol production from grass straw

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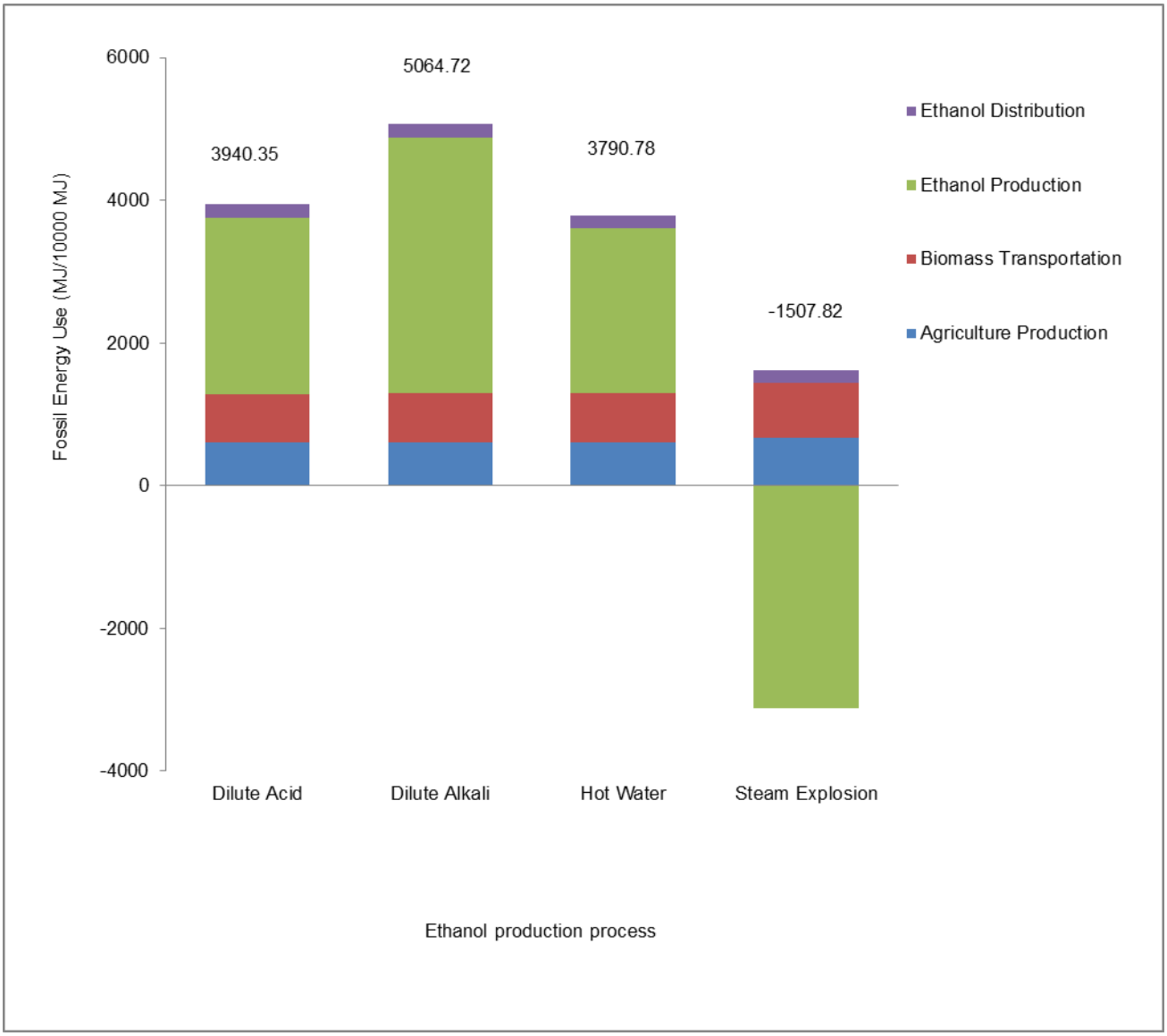

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622 **Figure 3** Fossil energy use per functional unit (10000 MJ ethanol energy) during various stages of life cycle of

623 ethanol

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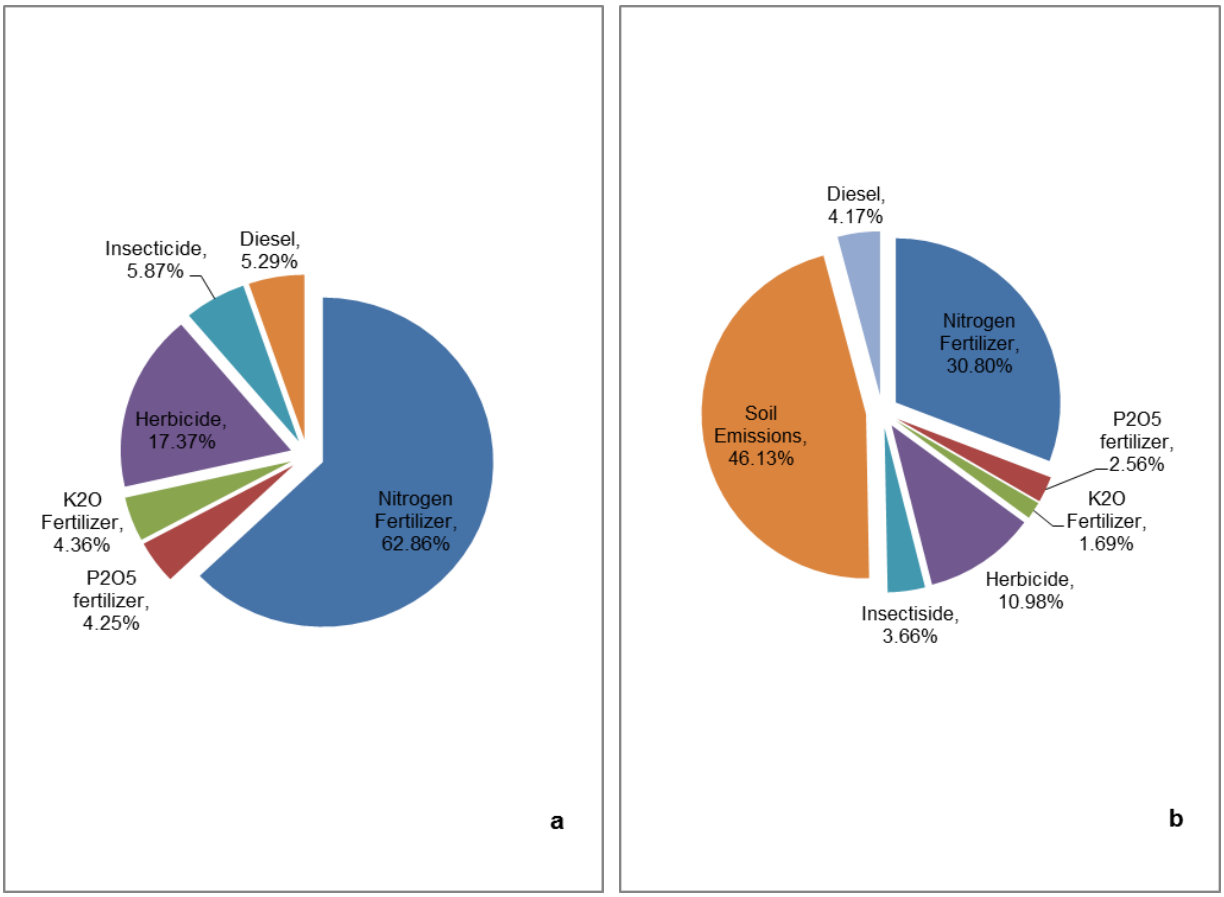


Figure 4 Fossil energy used and GHG emissions contribution from different inputs during grass straw production

(a) Fossil energy used (b) GHG emissions

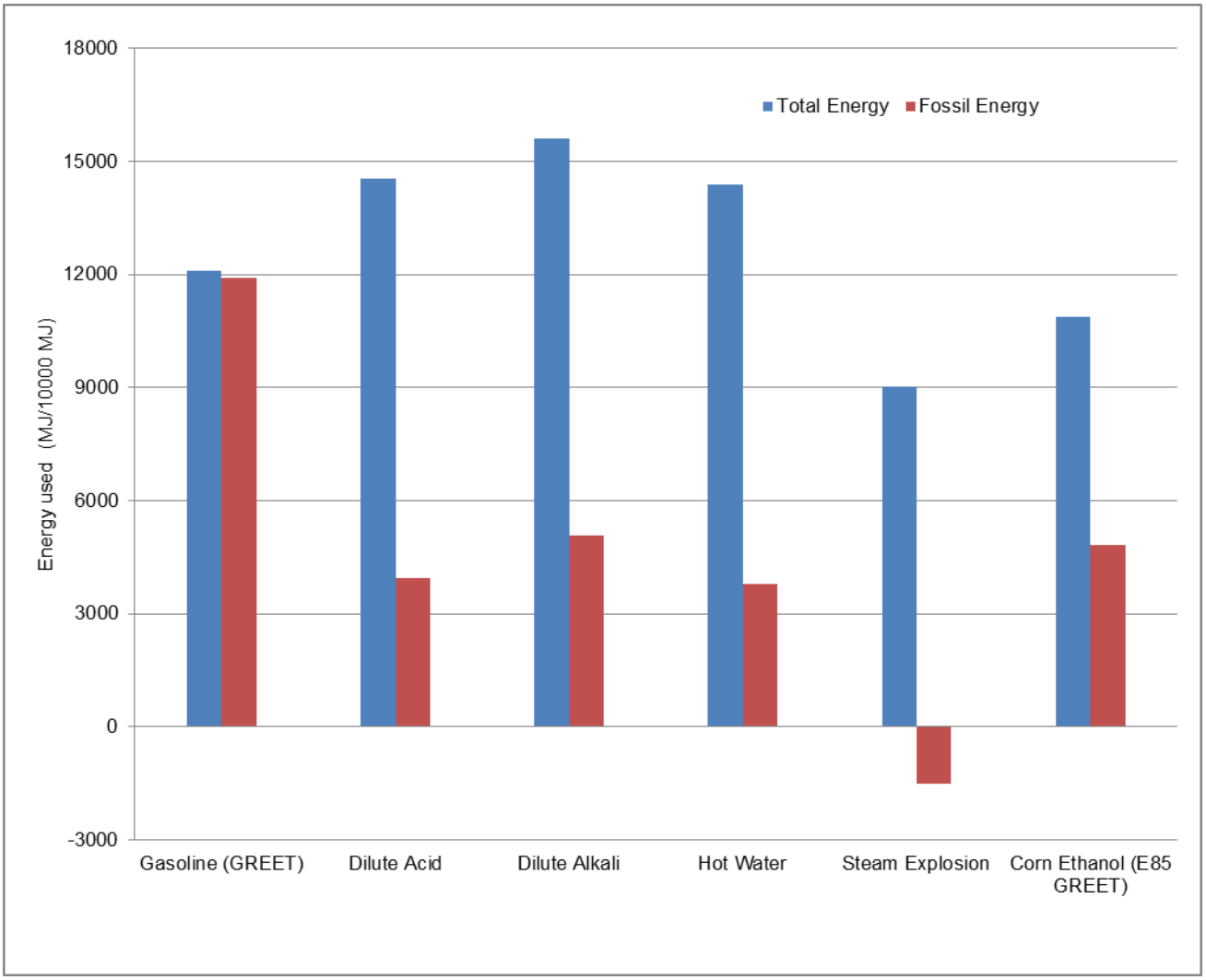
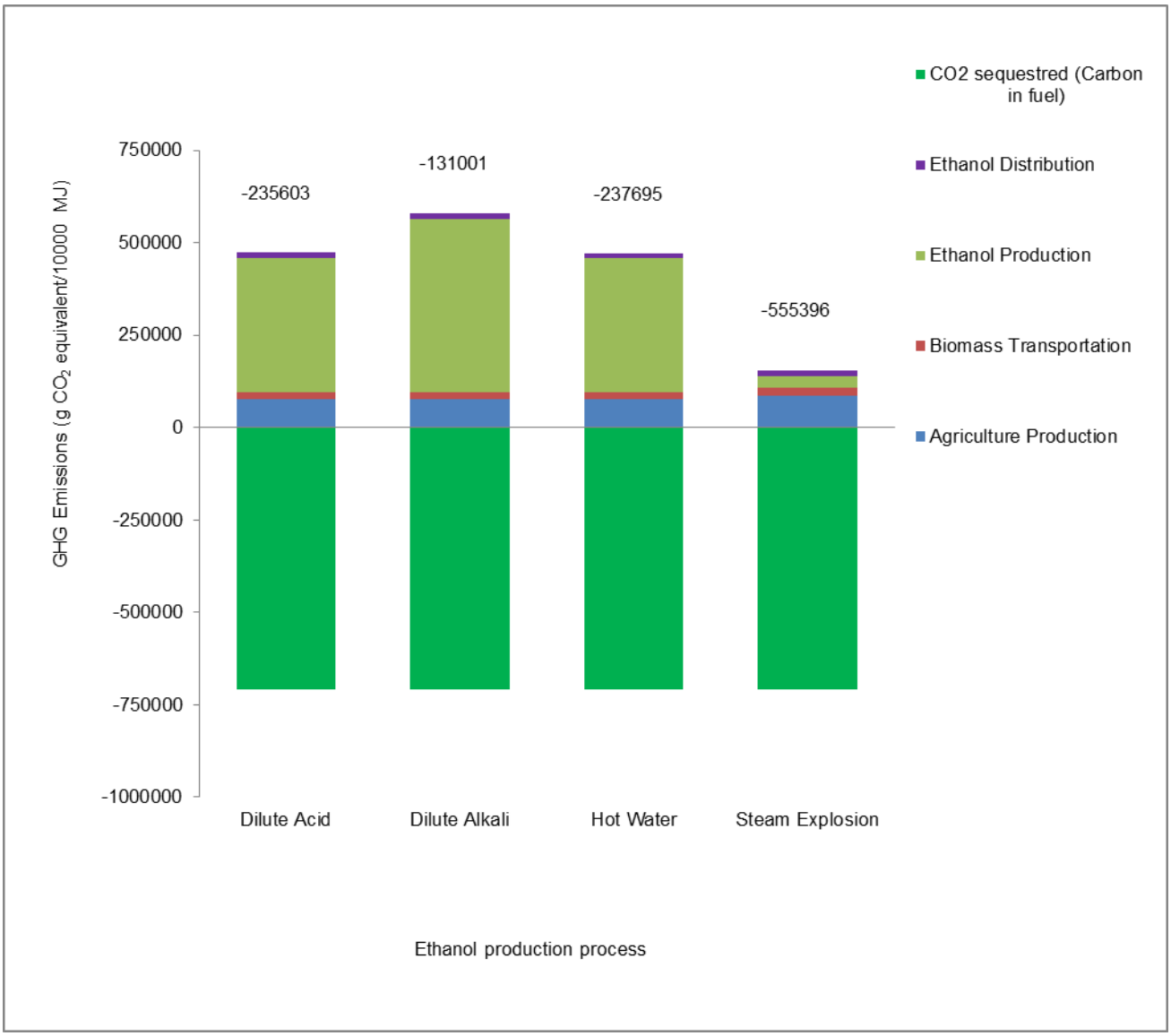


Figure 5 Total energy and fossil energy used for production of 10000 MJ of energy (1 functional unit) during life cycle of cellulosic ethanol, gasoline and corn ethanol



633

634 **Figure 6** GHG emissions produced per functional unit (10000 MJ ethanol energy) during various stages of life cycle
635 of ethanol

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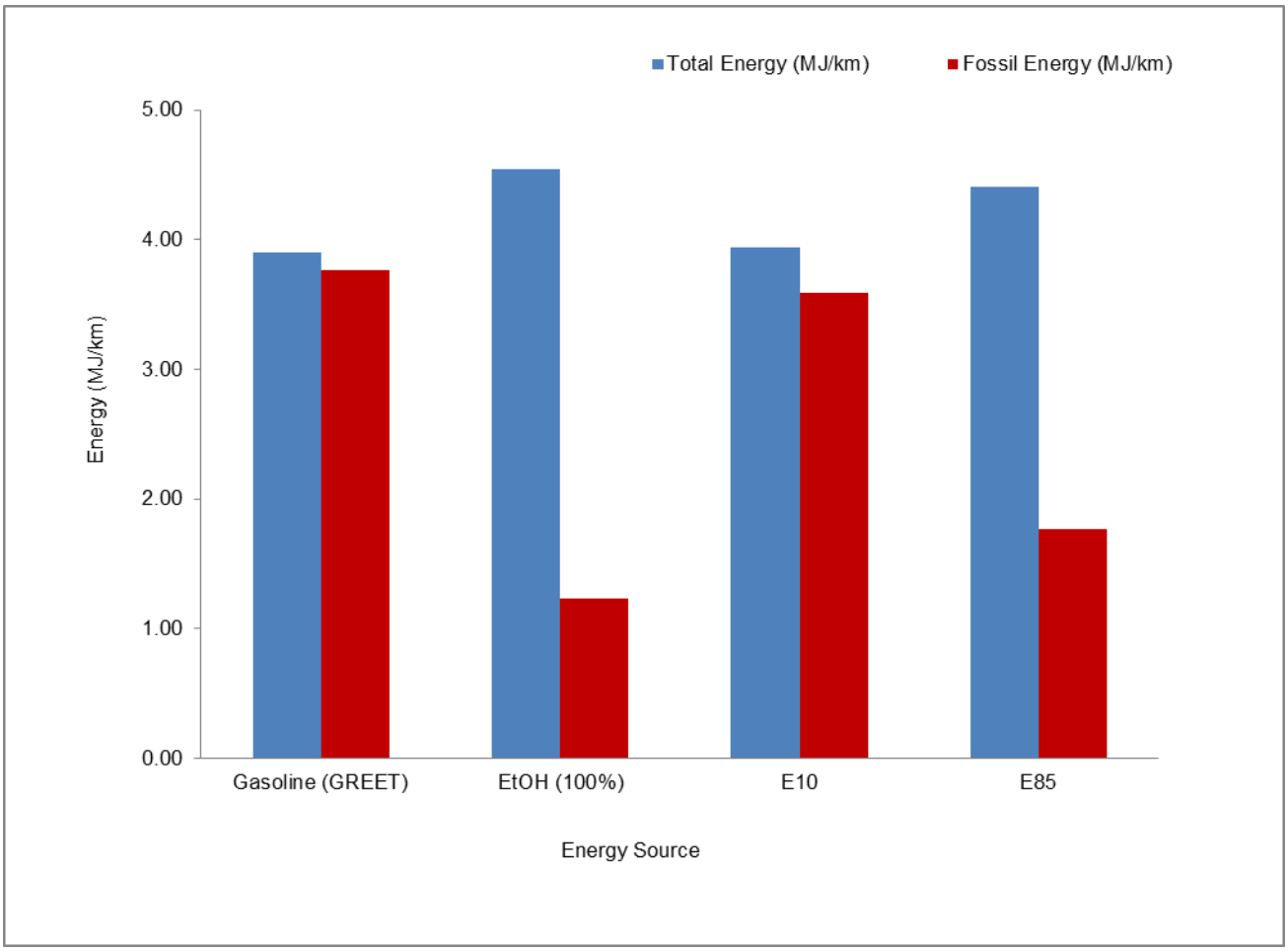
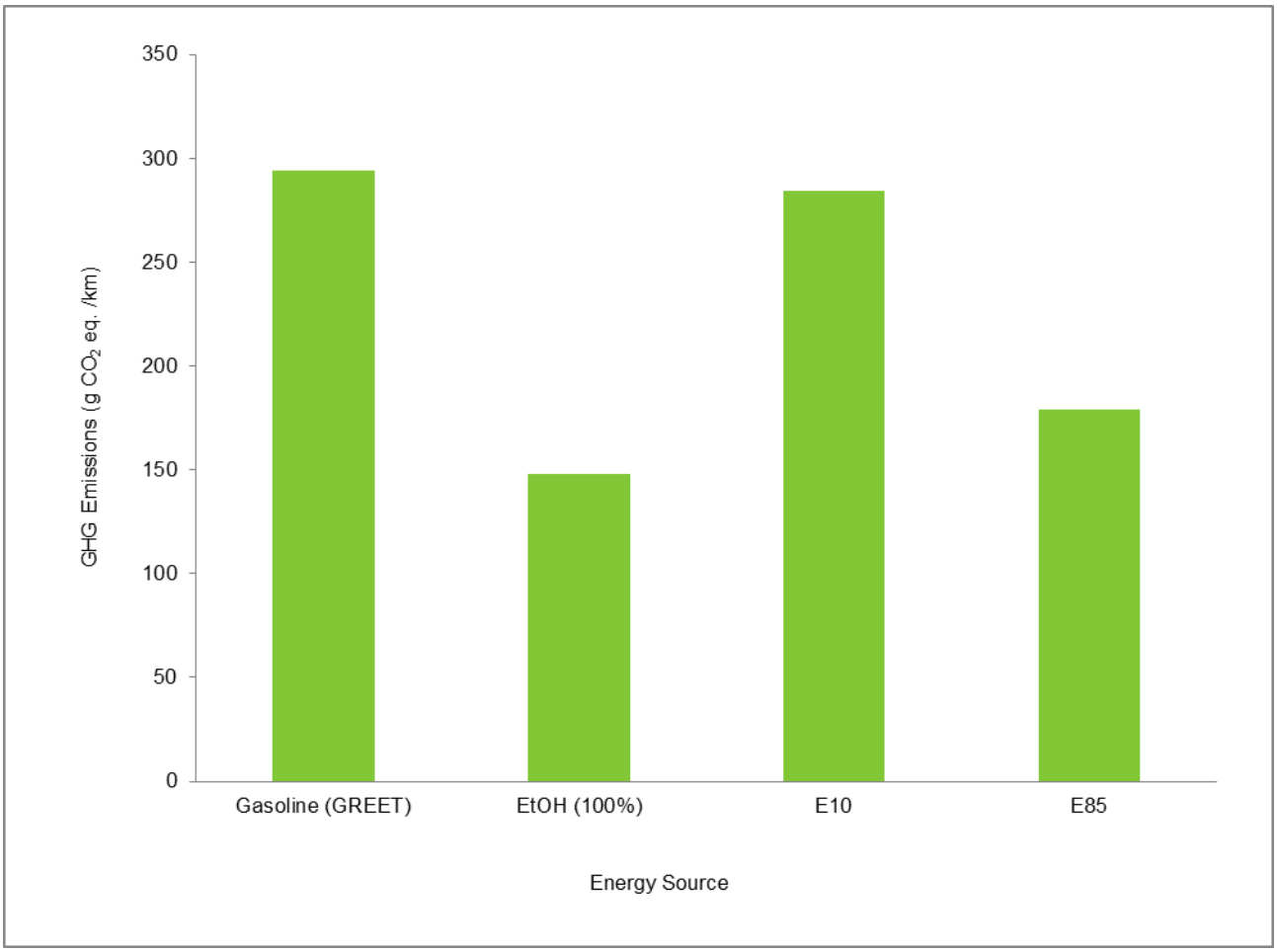


637

638 **Figure 7** Total energy and fossil energy used from life cycles of different fuel blends required for one km driving



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640 **Figure 8** GHG emissions produced from life cycles of different fuel blends required for one km driving

641