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Title: Economic feasibility and environmental life cycle assessment of ethanol production from lignocellulosic feedstock in Pacific Northwest U.S.

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Abstract

Bioethanol produced from the lignocellulosic feedstock is a potential alternative to fossil fuels in transportation sector and can help in reducing environmental burdens. Straw produced from perennial ryegrass (PR) and wheat is a non-food, cellulosic biomass resource available in abundance in the Pacific Northwest U.S. The aim of this study was to evaluate the economic viability and to estimate the energy use and greenhouse gas (GHG) emissions during life cycle of ethanol production from PR and wheat straw. Economic analysis of ethanol production on commercial scale was performed using engineering process model of ethanol production plant with processing capacity of 250,000 metric tons of feedstock/year, simulated in SuperPro

designer. Ethanol production yields for PR and wheat straw were estimated 250.7 and 316.2 L/dry metric ton biomass respectively, with total production capacity of 58.3 and 73.5 million liters of ethanol annually. Corresponding production costs of ethanol from PR and wheat straw were projected to be $0.86 and $0.71/L ethanol. Energy and emissions were calculated per functional unit of 10,000 MJ. Fossil energies were calculated as 4,282.9 and 2,656.7 MJ to produce one functional unit of ethanol from PR and wheat straw respectively. The GHG emissions during life cycle of ethanol production from PR and wheat straw were found to be 227.6 and 284.3 % less than those produced for 10,000 MJ of gasoline. Results from sensitivity analysis indicated that there is potential to reduce ethanol production cost by making technological improvements in pentose fermentation and enzyme production. These integrated economic and ecological assessment analyses are helpful in determining long-term sustainability of a product and can be used to drive energy policies in an environmentally sustainable direction.

Keywords: Bioethanol, ethanol production cost, grass straw, wheat straw, life cycle assessment, greenhouse gases, fossil energy

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I. Introduction

The global energy consumption is increasing and in year 2011, United States has been reported to consume a total energy of $1.02*10^5$ quadrillion joules. Most of this energy (82%) is derived from fossil energy sources such as petroleum, natural gas, coal and 9% comes from renewable sources [1]. Transportation sector accounts for nearly one third of total energy used worldwide and contributes about 21% of total greenhouse gas (GHG) emissions globally [2]. Increasing environmental concerns and depletion of fossil energy sources necessitate search for alternative renewable fuel sources that can reduce the GHG emissions and dependence on fossil fuels. Bioethanol, which can be produced from fermentation of sugars from starch or cellulose, has been considered as a potential alternative to gasoline as transportation fuel due to its compatibility with existing vehicles and potential to lessen the environmental burdens. There has been an eight fold increase in bioethanol production in the United States over last decade from 1770 to 13,900 million gallons, most of which can be attributed to the growth in the corn ethanol industry [3].

Many studies have raised concerns on the intensive use of fertilizers, pesticides and agricultural practices during the production of corn. These issues along with high feedstock prices, fresh water use, and food vs. fuel debate have necessitated the need to search for other alternative renewable resources for ethanol production. Ethanol produced from lignocellulosic feedstocks such as agricultural residues, grasses, forestry wastes, municipal solid wastes addresses some of these concerns and have been summarized elsewhere [4-7]. Lignocellulosic feedstocks are mainly composed of cellulose (20-50%), hemicellulose (15-35%), lignin (5-30%), extractives and proteins [8]. During biochemical conversion of lignocellulosic biomass to ethanol, cellulose and hemicellulose are hydrolyzed to sugar monomers, which are subsequently fermented to ethanol.

Cellulose, a polymer of long linear chains of glucose, is embedded in a complex matrix of hemicellulose and lignin, which decreases its accessibility to acids and enzymes. A pretreatment process is necessary to break the recalcitrant structure of biomass and enhance sugar yields during hydrolysis [6-9]. Several pretreatment strategies, broadly classified as physical (mechanical comminution); chemical (dilute acid, dilute alkali, aqueous ammonia); physicochemical (steam explosion, ammonia fiber explosion (AFEX), microwave-assisted acid alkali treatment); and biological pretreatment, have been developed and investigated on various lignocellulosic feedstocks [6-11]. Dilute acid pretreatment is one of the extensively investigated methods and has been found effective on various feedstocks [12]. The pretreatment process is highly energy intensive, which, along with high cost of enzymes and high transportation cost due to low energy density, increases the processing cost of lignocellulose to ethanol and limits the economic viability of the process on a commercial scale.

The use of locally grown lignocellulosic biomass can decrease the transportation cost and help to meet the rapidly growing demand of transportation fuels. Wheat and grass seed are two major crops grown in Pacific Northwest states: Oregon, Washington and Idaho. The grass seed industry in the Pacific Northwest U.S. produces more than 2 million ton per year of grass straw as a co-product and perennial ryegrass (*Lolium perenne* L.) is one of most common grass seed crops [13]. The Willamette Valley in Oregon is known as the "Grass seed capital" of the world and covers about 500,000 acres under grass seed production (~65% of total grass seed production in USA) [14]. Wheat is also one of the most abundant crops grown in Pacific Northwest. In 2012, states of Washington, Oregon and Idaho were reported to produce 302 million bushels of wheat harvested from 4.3 million acres [15] producing an estimated 8.2 million tons of wheat straw as a co-product [13]. Burning in field was the most common and economic practice to manage the straw, which

also aids in weed control and nutrient recycling. Since the new government regulations have restricted burning of biomass in the fields to control pollution, a large amount of the grass straw is exported each year to Asian countries from western Oregon [16]. These large amounts of straw that contain high amount of carbohydrates (up to 60%) could potentially be used for ethanol production and help in meeting regional fuel needs [17].

Long-term viability of using any feedstock for fuel production depends not only on its yield but also on the sustained production capacity, reduction in greenhouse gas emissions and net energy output. Life cycle assessment (LCA), an important tool used to assess impact of products, processes, and services on the environment, can play an important role in evaluating the environmental sustainability of the process. LCA can be used as a means to benchmark and compare different fuel alternatives objectively [18]. However, to realize the commercial viability of process, a techno-economic assessment is also necessary to establish capital and operating cost profile of the process [18]. As there are not as many full scale commercial operations for cellulosic ethanol production, comprehensive process simulation models can be used to perform material and energy flow in the production process and to estimate the production cost of ethanol.

The objective of this study was to perform an integrated techno-economic and life cycle assessment of ethanol production from perennial ryegrass (PR) and wheat straw in the pacific Northwest U.S. to evaluate the economic viability and environmental impact (in terms of fossil energy use and GHG emissions) of the process. The energy use and greenhouse gas emissions associated during the life cycle of ethanol production from these straws were estimated and compared with gasoline, corn ethanol and other studies on life cycle analysis of ethanol from lignocellulosic biomass. In addition to quantitatively examining the techno-economic feasibility and environmental impacts of the process, this analysis will help in identifying the key

operations/inputs in the bioethanol production life cycle. By identifying the processes/inputs with highest impact on overall process economics and environmental metrics, potential improvements in the process can be targeted.

II. Materials and methods

A. Biomass

Perennial ryegrass (PR) and wheat straw yields were assumed to be 8.4 [13] and 8.2 Mg/ha [14,19] respectively. The PR and wheat straws contain about 27% and 36% cellulose and 18% and 23% hemicellulose respectively on dry basis (figure 1), estimated based on previous studies [9,17]. Xylan is the major fraction (more than 80%) of hemicellulose in both PR and wheat straw [9,17].

B. Techno-economic analysis

A comprehensive techno-economic analysis was performed for conversion of straws into ethanol using detailed process model developed earlier by our group [10]. The model was developed using SuperPro Designer (Intelligen, Inc.) for an ethanol plant with a processing capacity of 250,000 metric tons of biomass per year.

1. Process model description

The ethanol production process consisted of five major processing sections: biomass preparation, pretreatment, simultaneous saccharification and co-fermentation (SSCoF), ethanol recovery and co-product recovery and utilization. The schematic representation of the process modeled to convert cellulosic biomass to ethanol is presented in figure 2. Biomass preparation included washing and size reduction steps. Pretreatment section was modeled for dilute acid pretreatment process with a subsequent detoxification step. Pretreatment was modeled for 20 % biomass loading. Operating conditions for the pretreatment of grass and wheat straw were set as: 1% w/w

of H_2SO_4 solution, 180°C temperature and 15 min residence time for grass straw; 0.5% w/w of H_2SO_4 solution, 170°C temperature and 30 min residence time for wheat straw [17]. Pretreated biomass was fractionated into solid and liquid streams using pneumapress filter. Liquid stream containing sugars from hemicellulose hydrolysis also contains many toxic compounds (e.g. furans from sugar degradation) formed during pretreatment process. These compounds inhibit the hydrolysis and fermentation processes and must be removed by the process of detoxification or conditioning. Overliming process consisting of pH adjustment to 10-12.0 using $Ca(OH)_2$ [20] and readjustment to 5.0-6.0 using H_2SO_4 was used for detoxification of the liquid stream. The precipitates formed during the process (mainly gypsum) were removed by hydrocyclone and filtration, and liquid stream is mixed with solids. Heat exchangers were placed wherever possible to maximize the energy efficiency of the process.

The SSCoF process consisted of simultaneous enzymatic hydrolysis of cellulose and hemicellulose and co fermentation of resulting hexose and pentose sugars. Sugars removed during pretreatment and enzymatic hydrolysis efficiencies of cellulose were obtained from laboratory studies [9,17]. Conversion efficiency of hemicellulose to sugar monomers during hydrolysis was assumed as 80%. The fermentation efficiencies of glucose and pentose sugars were assumed to be 95% and 70% respectively.

Downstream processing of ethanol production process model includes pure ethanol recovery, water treatment and use of lignin energy. Pure ethanol was recovered using distillation columns (combination of beer column and rectification column) followed by molecular sieves to produce anhydrous ethanol. The design, operating conditions and efficiencies of distillation system in the process model were based on cellulosic ethanol production model report by NREL [20] and Kumar and Murthy [10]. The spent stream from the distillation column devoid of ethanol was separated

into solid (lignin rich stream) and liquid fractions (mostly water and soluble solids) using pneumapress pressure filter. A fraction of liquid stream (25%) was treated in sequential anaerobic and aerobic digesters. Other fraction of liquid stream was concentrated in multiple-effect evaporator. The lignin rich stream, concentrated syrup from evaporator and biogas produced from anaerobic digestion were combusted in a fluidized bed reactor. The biogas production was during anaerobic digestion of waste water was estimated based on the detailed chemical oxygen demand calculations [21]. The condensate from the evaporator was recycled back as process water. Steam produced from combustor was used as process heat in plant and extra steam was used to produce electricity. A more detailed description of process model is provided elsewhere [10]. The models were used to conduct the detailed material and energy balances for the ethanol production plant and to estimate the capital costs, operating costs, chemicals and utilities used in the plant.

2. Assumptions for economic analysis

Year 2012 was used as the basis for all economic calculations. Biomass price including transportation cost was assumed to be $50 per metric ton for both wheat straw and perennial ryegrass. Costs of specific equipment (pretreatment reactor, pneumapress filter, fermenters, fluidized bed reactor, turbine/generator) for ethanol production process were calculated based on cost models of earlier process models of cellulosic ethanol [22,23] and corn ethanol [24-26]. The cost of equipment for current size were calculated using the exponential scaling equation (Eqn. 1) and cost of base equipment [20,22].

$$New\ cost = Original\ cost * \left(\frac{New\ size}{base\ size}\right)^{exp} \quad (1)$$

Costs of other equipment were calculated based on the built-in cost models in SuperPro designer. Installation costs of the equipment, and cost of utilities and consumables were estimated from the

recent techno-economic studies [23,25]. Detailed assumptions used in the process models to calculate direct cost, indirect cost and direct fixed cost are provided elsewhere [10].

C. Life Cycle Analysis

A comprehensive well-to-pump LCA was performed to investigate the overall net energy balance and GHG emissions during ethanol production from wheat straw and PR straw.

1. Process description

The overall well-to-pump LCA model was divided into four main sections: agricultural production, biomass collection and transportation, ethanol production, and ethanol distribution. A functional unit of 10,000 MJ of energy from ethanol was chosen for the analysis and all results in terms of energy use and GHG emissions are presented per functional unit. As all fuels are not equal on volumetric or mass basis (e.g. 1L of ethanol is not equivalent to 1L of gasoline), choosing functional unit in terms of energy provides equivalence between products (10,000 MJ of energy of ethanol is same as that of gasoline) and helps in direct comparison among different liquid fuel alternatives.

To calculate the distance required for biomass transportation, ethanol plant was assumed in the center of farmland and the radius of circle (one way distance) was calculated. The required area was calculated by using Eqn. 2 based on the biomass demand ($D_{biomass}$) and accounting the winding factor by including biomass yields ($Y_{biomass}$), fraction of area under agriculture ($F_{cropland}$), fraction of agricultural land under required crop (F_{avail}) and fraction of biomass that can be removed without affecting the soil quality ($F_{collect}$) (assumed 50% in current study) [20]. Biomass is transported by heavy duty trucks and trucks were considered to be going empty one way.

$$Area = \frac{D_{biomass}}{Y_{biomass} * F_{cropland} * F_{avail.} * F_{collect}} \quad (2)$$

Assuming 60% area under agriculture and 0.75 value for F_{avail}, the distances required were calculated as 20.6 km and 20.9 km to supply 250,000 Mt/year of perennial ryegrass and wheat straw respectively.

2. Data inventory and assumptions

Data inventory is a critical step in the LCA studies. Data on agricultural production such as crop yields, amounts of fertilizers and herbicides used, insecticides used, fuel used in the machinery used, and seed application, were specific to the state of Oregon and collected from Oregon Enterprise budget [19], published research papers [13] and local farmers in Oregon (Rose Agriseeds, Inc.). Data related to ethanol production processes (process inputs): amount of material (e.g. chemicals, enzymes, yeast) and utilities (e.g. steam, electricity, cooling water) used, ethanol yields, and energy from co-products were obtained from process model simulations described earlier. Most of the data related to energy use and emissions during production of chemicals, utilities, production and use of other fuels (e.g. diesel, gasoline), and fuel efficiencies of transportation vehicles were collected from Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) 1.8d model [27] and the U.S. life-cycle inventory database [28]. Some specific data related to cellulosic ethanol production (e.g. production of enzymes) were obtained from published reports and research papers [23,29].

Grass seed is a perennial crop and stand life of the crop was assumed three years (one established year and two harvesting years) and data on biomass yields, agricultural inputs (different in establishment year and harvesting years) were averaged over three years and used in the analysis. All biomass cannot be removed from the field; only 50% of straw was assumed to be collected from the field without affecting the soil quality. Emissions (N_2O emissions) from the soil due to nitrogen fertilizer application were assumed 1.5% of nitrogen in fertilizers applied, same as for

switchgrass [30,31]. Due to lack of specific data available, energy use and emissions during biomass collection were assumed same as for corn stover (313.7 MJ/Mg biomass fossil energy and 6.7 kg CO_2 equivalent emissions per Mg of biomass) as calculated by Sokhansanj et al. [32]. Cellulase enzymes were assumed to be purchased from commercial sources at a protein concentration of 10% and 60 FPU/g enzyme broth activity [23]. The thermal efficiency of boiler during steam generation from the lignin residues (co-product) were used 75% [33, 34] and conversion efficiency of biomass energy to electricity was assumed to be 30% for the analysis. During energy analysis, lower heating values (LHV) of fuels were used, which is more appropriate for energy calculation in vehicle applications [35]. Default values of GREET model were used for ethanol distribution.

3. System boundary and co-product allocation

Choice of system boundary in LCA is very critical and is one of the major reasons for having different results from LCA of the same process in different studies. Various approaches such as mass based, energy based or heuristics based selection of important processes, have been used for boundary selection in various studies. In this study, relative mass, energy, and economic value (RMEE) method was used to select the system boundary. The RMEE approach suggested by Raynolds et al [36], is a comprehensive method and includes a unit process in boundary based on ratios of mass, energy and economic value of the product to those of functional unit chosen in the study. If any of the three ratios for an input exceeds the predefined cut off value (5% in current study), the upstream unit process of that input is included in the system boundary. Certain inputs do not have large mass flow in the process, however have significant economic value or carry huge energy value with them. The RMEE method makes sure that such items are included in the analysis and avoids any arbitrary exclusion of an item [36-38].

The co-product allocation method is another major selection that can significantly influence the results of life cycle analysis and should be chosen carefully [39]. There are two multiproduct processes in the ethanol production cycle: straw and crop, and ethanol and lignin energy. Grass straw is a co-product of grass seed production; therefore, energy use and emissions during agricultural production were allocated between grass seed and straw using economic based allocation method. Steam and electricity produced from lignin residues are co-products in ethanol production process. System expansion (displacement) approach [39] was used to calculate co-product credits, which assumes that the steam and electricity produced from lignin residue replace the process steam and electricity required for the plant operations and offset the energy use and GHG emissions to produce these utilities using fossil fuels. The emissions were calculated in terms of gram CO_2 equivalent using global warming potential factors of 1, 25 and 298 for CO_2, CH_4 and N_2O respectively [27].

The data collected from different sources for all sections of the system were organized in Microsoft Excel spreadsheets and analysis was performed. Most of the data (e.g. production of chemicals, utilities) used in the study were specific to USA.

III. Results and Discussion

A. Process Economics and Energy use

Models of ethanol production plant with annual biomass processing capacity of 250,000 metric tons were simulated in SuperPro Designer. The ethanol yields from process simulations were estimated 250.7 and 316.2 L/dry metric ton (66.2 and 83.5 gal/dry metric ton) of PR and wheat straw respectively. The ethanol production yield from PR straw was comparatively lower mainly due to lower carbohydrate content in PR (45% vs. 59% in dry wheat straw).

1. Economics of ethanol production

The capital costs of ethanol production plants were estimated as 127 and 122.6 $MM with total ethanol production capacities of 58.3 and 73.5 million L/year (15.4 and 19.4 million gal/year) for PR and wheat straw respectively. Overall economics of the process are presented in table I. Other than purchase and installation cost of equipment, capital cost included cost of piping, buildings, and other indirect costs (e.g. construction cost, engineering cost). The installed equipment cost (1.2 and 0.94 $/L ethanol for PR and wheat straw) accounted for about 56% of total capital costs in both cases.

The calculated capital cost, $2.13/L ethanol for PR straw was higher than $1.67/L ethanol for wheat straw in current study and $1.92/L ethanol produced from Tall fescue (TF) straw (another variety of grass seed crop) calculated in our earlier study [10]. Kazi et al. [23] conducted the economic analysis of ethanol production plant using corn stover as feedstock and estimated about $1.86 /L ethanol capital cost using dilute acid pretreatment. Capital cost for ethanol production from PR straw was higher as compared to wheat straw, corn stover and TF because of relatively lower ethanol yields which can be attributed to lower fermentable sugar content in PR: 250.7 L/Mg of PR vs. 316.2, 289 and 256.6 L/Mg of wheat straw, corn stover and TF respectively. The ethanol production yield was relatively high from wheat straw, which resulted in the lower capital cost per unit ethanol produced.

Unit cost of ethanol production from PR and wheat straw were estimated as $0.86 and $0.71/L ($3.25 and $2.70 per gallon) of ethanol. While the production cost estimates for PR straw were similar to the reported values TF ($0.84/L ethanol) and corn stover ($0.91/L ethanol), they were higher than the switchgrass ethanol costs ($0.45/L ethanol) reported by Laser et al. [10, 22, 23] using dilute acid pretreatment method.

Breakdown of operating cost as facility dependent costs, raw material costs and other costs (labor, utilities and waste disposal) for the ethanol production processes are illustrated in figure 3. Raw material accounted for about 42% and 45% of total operating cost for ethanol production from PR and wheat straw respectively.

The amounts and costs of bulk materials used in the ethanol production process are given in table II. Biomass price (21.5 and 17 ¢/L ethanol for PR and wheat straw respectively) was major contributor in the total bulk material cost followed by enzyme cost (11.16 and 12.79 ¢/L ethanol for PR and wheat straw respectively) in both cases. Biomass cost per unit ethanol for wheat straw was found similar to that of switchgrass (58.3 ¢/gal in 2009 dollars) as estimated by Laser et al. [22]. Enzyme cost accounted for 31% and 39.8% of total material cost during ethanol production from PR and wheat straw respectively and highlights the importance of strategies to reduce overall enzyme cost for commercialization of cellulosic ethanol[23, 40-42]. Enzyme cost was about 15% higher in case of wheat straw than that of PR straw due to higher enzyme usage due to higher cellulose content of wheat straw. In current model, enzyme loading and the cost of enzyme broth (10% protein in broth and 600 FPU/mg protein) were assumed to be 15 FPU/g cellulose and $0.517/kg of enzyme broth respectively [10, 23]. Enzyme cost of wheat straw is similar to the enzyme cost during ethanol production from TF straw (13.52 ¢/L ethanol) estimated in our earlier study [10]. Although cellulose content was relatively higher in wheat straw (36% vs. 31% for TF straw), enzyme cost per unit ethanol was a little lower due to higher ethanol yield (316.2 vs. 256.62 L/dry metric ton for PR straw).

2. Process energy

Ethanol production from lignocellulosic biomass in general are highly energy intensive due to use of large amounts of process heat in form of steam (low pressure (LP) steam at 152°C and

502 kPa and high pressure (HP) steam at 242°C and 3464 kPa) and electricity during pretreatment process [10, 20, 43, 44]. Annual usage and cost of utilities during ethanol production from PR and wheat straw are summarized in table III. To maximize the heating efficiency, HP steam is usually recycled for LP applications before the condensate is returned to boilers. In the current study, it was assumed that 50% of the HP will be reused in LP applications in current analysis. Lignin rich residues remaining after fermentation are used to produce process steam in the cellulosic ethanol plant and in most of the cases steam production exceeds the requirement of plant [10, 20, 22, 23]. Similar results were obtained in current study, where lignin energy was sufficient to supply the steam required (table IV) and hence the cost of steam was adjusted to zero for economic analysis. No other economic credit was assigned to lignin residues as all of the lignin along with biogas produced from anaerobic digestion of waste water was considered to be used for on-site production of steam and electricity.

The amounts of steam used during the ethanol production (6.4 and 5.6 kg/L ethanol for PR and wheat straw respectively) were comparable to steam requirement (4.42 kg/L ethanol) calculated by Aden et al [20]. Although total thermal energy usage was higher in case of wheat straw (table III), amounts used per unit ethanol are lower than those of PR straw (table IV) due to higher ethanol yield per ton of biomass. It can be observed from table IV that lignin energy can supply about 140% and 159% of the steam demand during ethanol production from PR and wheat straw respectively. The excess steam was used to produce electricity. Electricity production potential was estimated 2.42 and 3.122 kWh/gal of ethanol produced from PR and wheat straw respectively, assuming 30% conversion efficiency to electricity. It should be noted that lignin energy values presented in table IV were calculated not only from lignin residue stream from distillation columns but also including concentrated syrup from multi-effect evaporator and

biogas from anaerobic treatment of waste water. Lignin rich stream obtained after ethanol purification carries high percentage of water (~55%). Lignin energy values in table IV were calculated after deducting the energy required to remove this moisture from total available energy.

3. Ethanol cost sensitivity

Biomass price is another major contributor in overall economics of the process. Biomass price and enzyme cost were major contributors to the ethanol cost. A sensitivity analysis was performed to study the impact of biomass and enzyme price on the ethanol production cost. The ethanol cost was calculated from process simulations by varying the straw price from $25 to $100/metric ton for both PR and wheat (figure 4). Ethanol production cost was estimated as $4.06 (25% increase) and $3.35 (24% increase) for PR and wheat straw respectively at biomass price of $100/metric ton. There was 12.6 and 11.9% decrease in production cost by changing the biomass price to $25/metric ton for PR and wheat straw respectively. At biomass price of $100/metric ton, the operating costs changed to 65.03 and 62.50 $ MM from 52.53 and 50.00 $ MM at biomass price of $50/metric ton (base case) for wheat straw and PR straw respectively (figure 4).

Sensitivity of enzyme costs on ethanol price was investigated by changing the enzyme cost to half and double than that of base case ($0.517/kg). For PR and wheat straw, increase in the ethanol cost was 12.9% and 18.1% respectively when the enzyme costs were doubled ($0.517/kg to $1.034/kg). A reduction of enzyme price by 50% ($0.517/kg to $0.259/kg) resulted in 6.5 and 8.9% decrease in the ethanol price cost for PR and wheat straw respectively. The effect of enzyme cost was higher in case of ethanol produced from wheat straw, due to higher enzyme dosages used.

Fermentation of pentose sugars (mainly found in hemicellulose) is a big challenge in the cellulosic ethanol production process and has significant impact on ethanol yield and overall economics of the process. Commercially used yeast strains for corn ethanol are not very effective in converting pentose sugars. There is an on-going research on genetically modified strains which can effectively ferment both pentose and hexose sugars [45-47]. Sensitivity of ethanol cost was investigated by varying the pentose fermentation efficiency from 30 to 90% (70% was assumed in base case) (figure 5). At 90% fermentation efficiency (assumed for techno-economic analysis by Laser et al 2009 [22]), the ethanol production cost was determined $2.96 and $2.52/gal ethanol produced from PR and wheat straw respectively.

B. Life Cycle Energy Use and GHG Emissions

The complete system illustrating all processes included in this well to pump or field to pump LCA study of ethanol production from PR and wheat straw is presented in figure 6. All results were calculated on basis of functional unit of 10,000 MJ of ethanol energy (470.05 L or 371.03 kg of ethanol) at the pump.

1. Life cycle energy analysis

Fossil energy use during life cycle of ethanol production from PR and wheat straw were 4282.9 and 2656.7 MJ per 10000 MJ of energy produced (functional unit), which were about 64 and 78% less than that from GREET life cycle analysis for gasoline (figure 7). Energy produced from co-product (lignin and biogas) was deducted from total energy used during ethanol production process.

Although not surprising, it is interesting to note that total energy used (14905.4 and 13166.1 MJ per 10000 MJ) during the life cycle were higher than that of gasoline (12104.5 MJ per 10000

MJ). Total energy input in both cases is higher than that of energy produced. The results found here are similar to results reported by Wang 2005 [48] for life cycle of cellulosic ethanol. Fossil energy accounts from energy produced from non-renewable sources: coal, natural gas and petroleum, whereas total energy includes energy from both fossil and renewable sources.

It can be observed from the figure 7 that ethanol production process had major contribution in the total fossil energy used in the life cycle of cellulosic ethanol production. Thermal energy use, electricity consumption, and energy produced from co-products per 10,000 MJ of ethanol energy (functional unit) during ethanol production process are presented in table V.

Net energy value (NEV) and net energy ratio (NER) are common terms used in LCA studies to assess the energy efficiencies and fossil fuel displacement values. NEV and NER were calculated using Eqns. 3 and 4 respectively. Positive value of NEV and NER value above 1.0 indicates the energy gain in terms of fossil energy, i.e. energy content of the fuel was more than the fossil energy used to produce that fuel.

$$\text{Net Energy Value} = \text{Energy in functional unit} - \text{energy use to produce functional unit} \quad (3)$$

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

Net energy value of ethanol production from PR straw and wheat straw were found to be 5,717.1 and 7,363.9 MJ per 10,000 MJ energy (12.2 and 15.7 MJ/ L ethanol) respectively. The NEV values were comparable to the values for ethanol production from tall fescue straw (12.9 MJ/ L ethanol) estimated in our earlier study [38], switchgrass (21.5 MJ/L ethanol) assessed by Schmer et al. (2008) [49]. These values were positive as opposed to negative NEV value for gasoline (-1,869.1 MJ/ 10,000 MJ). The NER values were estimated as 2.34 and 3.8 for ethanol production from PR straw and wheat straw respectively. The NER values from the current study and their

comparison to the energy ratios of gasoline, corn ethanol and other cellulosic ethanol studies in the literature are presented in the figure 8.

The value of NER was less than one for gasoline indicating that the fossil energy input is higher than the energy in the fuel. It is important to note that different fuels cannot be compared solely based on the NER values as different fuels have different energy quality (e.g. one MJ of coal is not equivalent to 1 MJ of electricity) [50]. The comparisons can be made among the fuels of equal quality only. All values shown in figure 8 are for ethanol and gasoline which are equivalent in terms of energy quality.

2. Life cycle GHG emissions

The GHG emissions during life cycle of ethanol production from PR and wheat straw were estimated to be -282.7 and -329.2 kg CO_2 equivalent per 10,000 MJ of ethanol (-485.1 and -700.5 g CO_2 equivalent/ L ethanol) respectively. The GHG emissions for PR and wheat straw were found 227.6 and 284.3 % less than those produced during life cycle of gasoline (GREET default). The contribution of various stages during life cycle of ethanol production to total GHG emissions is illustrated in figure 9.

The values of GHG emissions were found negative because of co-product energy available during ethanol production process, which displaces the GHG emissions produced by fossil fuels required to produce steam and electricity in the plant. The CO_2 released during fermentation and lignin burning was not accounted as this CO_2 was sequestered from environment by photosynthesis process during biomass production (figure 10). In this study, it was assumed that no net CO2 was sequestered into the soil and net soil carbon remained same. The CO_2 sequestered was also calculated from carbon in ethanol and was subtracted from the total LCA emissions during well to pump analysis [48], but was included in well to wheel analysis presented

later in the paper. Similar negative values were obtained by Spatari et al [51] from LCA of ethanol production from switchgrass (−1,020 CO_2 eq./L ethanol) and corn stover (−1,179 g CO_2 eq./L ethanol) (-479.5 and -554 kg CO_2 eq./10,000 MJ of ethanol from switchgrass and corn stover). The differences in values are due to different agricultural inputs, ethanol yields and assumptions for process efficiencies. The GHG emissions for PR straw were about 11% higher than those for TF straw (-228 vs. -255.6 kg CO_2 eq./10,000 MJ of ethanol), estimated in our previous study [38]. This difference was mainly due to relatively higher ethanol yield from TF straw (250.7 vs. 256.7 L/dry ton biomass).

Ethanol production process was major contributor in total GHG emissions during whole life cycle of ethanol followed by agricultural production activities. Although most of the emissions related to energy required during the process are displaced by using lignin energy, a large amount of emissions are associated with production of chemicals and enzymes. As there are continuous developments in the cellulase enzymes and their production technologies, a great variation is found in the emission data related to enzyme production. In the current study, value of 2,264 g CO2 eq./kg enzyme produced, reported by Maclean and Spatari 2009 [29], was assumed for analysis. The GHG emissions associated with cellulase enzymes (50.3 and 72.8 g/kg PR and wheat straw respectively) were estimated to be 229.8 and 263.3 kg CO2 eq./10,000 MJ of ethanol produced from PR and wheat straw respectively. The values were comparable to those of TF straw (278.3 CO2 eq./10,000 MJ of ethanol).

Contribution of various inputs and activities to total fossil energy use and GHG emissions during agricultural production of biomass are presented in table VI and figure 11. The values presented in the table V correspond to straw production after allocation between straw and crop grains on economic basis. Major fractions of the total fossil energy and GHG emissions during biomass

production are associated with production and use of nitrogen fertilizers. Nitrogen fertilizer production was responsible for about 58 and 67% of total fossil energy used during production of PR and wheat straw respectively (figure 11).

Fossil energy associated to herbicide production was second major contributor (18.8%) for PR straw production, whereas it accounted only 8% of total fossil energy during wheat straw production. Production and use of nitrogen fertilizer resulted in 72.2% (29% from production and 43.3% due to N_2O emissions from soil) and 77.8% (31% from production and 46.7% due to N_2O emissions from soil) of total GHG emissions during PR and wheat straw production respectively.

3. Well to wheel analysis

LCA results were also evaluated for well to wheel or field to wheel analysis that accounts for energy use and emissions during vehicle operation also. The analysis was performed for pure ethanol and two blends: E10 (10% ethanol and 90% gasoline) and E85 (85% ethanol and 15% gasoline). The results were evaluated considering ethanol use in a midsize car, with fuel efficiency of 0.32 km/MJ of fuel (gasoline, ethanol, and ethanol blends) [52]. Fossil energy used during life cycle of E10 and E85 to drive 1 km were calculated 3.6 and 1.8 MJ respectively (4.4 and 50.8 % less than that of gasoline respectively).

The GHG emissions were estimated 180.9 and 155.3 g CO_2 equivalent per kilometer driving with E85 produced from PR straw and wheat straw respectively (38.5 and 47.2% less than that of gasoline respectively). The results were similar to as observed by Spatari et al 2005 [51] for life cycle of ethanol production from switchgrass and corn stover (about 57% and 65% less GHG emissions per kilometer driving by ethanol instead of gasoline) (figure 12).

4. Sensitivity analysis

Life cycle analysis results are impacted by selection of system boundary, assumptions used, uncertainties in collected data and especially, co-product allocation method [53-55]. A sensitivity analysis was performed by changing the co-allocation method during agricultural production (mass based allocation instead of economy based allocation between crop grain and straw). Mass based biomass to seed ratios for perennial ryegrass and wheat are 4.4 and 1.6 respectively, whereas economic values of straw from PR and wheat are 0.18 and 0.48 times those of their respective seeds/grains. By using mass based allocation, fossil energy use and GHG emissions during life cycle of ethanol increased by 29.7 and 32.2% respectively for wheat straw. This increase was highly noteworthy in case of PR straw, where fossil energy used was more than double (109.3% increase) and GHG emissions increased by about 256%. The increase was relatively higher in case of PR straw because of high biomass/seed ratio and very low economic value of biomass relative to the main crop. The allocation ratio between PR straw and grass seed shifted from 0.18 to 4.4 with change in allocation method from economy to mass basis and hence now grass straw shared about 68.7% of fossil energy used and GHG emissions produced during agricultural production. Similar results were obtained for TF straw (62.4% and 133.1% increase in fossil energy and GHG emissions respectively) in our earlier study [38] and for corn stover by Luo et al 2009 [53] (shift of 1.7–7.5 in corn/stover allocation ratio by changing allocation method to economic value instead of mass/energy).

Additional analysis was performed by changing the biomass energy to electricity conversion efficiency (assumed 30% for base case). Increasing this efficiency will result in more electricity production from lignin (renewable source) and displace GHG emissions due to fossil fuel burning to produce electricity. GHG emissions increased by 15.9% and decreased by 31.7% with

change in conversion efficiency to 25% and 40% respectively for PR straw. The changes of 14.15 and -28.3% were observed for wheat straw after changing efficiency to 40% and 25% respectively.

IV. Conclusion

A comprehensive techno-economic and life cycle analysis was performed to evaluate the economic feasibility and environmental footprints of ethanol production from wheat straw and perennial ryegrass straw. The ethanol production costs from PR and wheat straw were estimated $3.25 and $2.7 per gallon of ethanol. Major fractions of the raw material costs were found to be associated with biomass and cellulase enzymes. There is a potential to reduce ethanol cost by improving pentose sugar fermentation and yield of ethanol from biomass. Energy produced from lignin residue during ethanol production was found sufficient to provide the process heat in the plant. Fossil energies used during life cycle of ethanol production from PR and wheat straw were found 64 and 78% less than that from gasoline (Net energy ratios of 2.3 and 3.8 for PR and wheat straw). The life cycle GHG emissions were determined -282.7 and -329.2 kg CO_2 equivalent per 10,000 MJ of ethanol for PR and wheat straw respectively. Production and use of nitrogen fertilizers accounted for more than 70% of total GHG emissions during agricultural production of PR and wheat. The LCA results were highly sensitive to allocation method used for distribution of energy and emissions among straw and main crop, especially for grass straw which has high biomass productivity and very low relative economic value. Techno-economic and life cycle assessments indicated that production of ethanol from PR and wheat straw is competitive to other alternatives to ethanol production.

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Tables

Table I. Overall economics of the ethanol production from the plant with 250,000 metric ton/year biomass processing (2012 prices)

	PR Straw	Wheat Straw
Total Investment (MM $)	127.02	122.63
Operating Cost (MM $/yr)	50	52.53
Ethanol (MM gal/yr)	15.395	19.424
Ethanol Unit Cost ($/gal)	3.25	2.70
Direct Fixed Capital[1] (MM $)	115.46	113.89
Equipment Cost (MM $/yr)	49.27	48.56
Installation (MM $/yr)	20.78	20.6

[1] DFC includes direct cost (equipment, installation, piping etc.), indirect cost and other costs (contractors' fees and contingency costs)

Table II. Bulk material amount and cost during ethanol production from the plant with 250,000 metric ton/year biomass processing (2012 prices)

		PR Straw		Wheat Straw	
Material	Unit Cost ($/kg)	Amount (kg 1000X)	Cost (¢ /L EtOH)	Amount (kg 1000X)	Cost (¢ /L EtOH)
Biomass	0.050	250000	21.45	250000	17.00
Sulfuric Acid	0.035	12255.48	0.74	7702.27	0.37
Ca Hydroxide	0.100	5967.72	1.02	3078.45	0.42
Diammonium Phosphate (DAP)	0.210	79.20	0.03	79.20	0.02
Cellulase	0.517	12583.34	11.16	18193.10	12.79
Yeast	2.300	198.00	0.78	198.00	0.62
Gasoline (Denaturation)	0.800	476.77	0.66	601.31	0.82

Table III. Amount and cost of overall utilities used in ethanol making process from the plant with 250,000 metric ton/year biomass processing

	PR Straw			Wheat Straw		
Utility	Annual Amount (10^6 X)	Amount (kg/L EtOH)	Cost (¢ /L EtOH)	Annual Amount (10^6 X)	Amount (kg/L EtOH)	Cost (¢ /L EtOH)
Electricity* (kWh)	33.36	0.57	4.01	33.97	0.46	3.23
Steam (kg)	346.09	5.94	0.000	384.72	5.23	0.00
Cooling Water (kg)	29537.08	506.91	2.54	33668.88	457.97	2.29
Chilled Water (kg)	35.02	0.60	0.02	50.63	0.69	0.03
CT water (kg)	5295.75	90.89	0.64	5295.75	72.03	0.50
Steam (High P) (kg)	25.15	0.43	0.000	29.41	0.40	0.00

* Electricity values did not account for power required for cooling and chilled water

Table IV. Process steam demand and lignin energy available during ethanol production in the plant with 250,000 metric ton/year biomass processing

Biomass	Steam demand (kJ/ L EtOH)	Lignin Energy (kJ/ L EtOH)	Excess Lignin Energy (kJ/ L EtOH)	Electricity potential (kWh/ L EtOH)
PR Straw	19127.80	26814.01	7686.21	0.64
Wheat Straw	16883.26	26780.76	9897.50	0.82

Table V. Ethanol yield and energy analysis during ethanol production process

	PR Straw	Wheat Straw
Ethanol Yield (L/dry ton biomass)	250.65	316.24
Thermal Energy (MJ/10000 MJ)	8990.82	7935.79
Electricity (kWh/10000 MJ)	442.19	373.57
Co-Product Energy (MJ/10000 MJ)	12603.83	12588.23
Electricity Produced (kWh/10000 MJ)	301.07	387.68

Table VI. Contribution of various inputs during agricultural production

	PR Straw			Wheat Straw		
	Total Energy (MJ)	Fossil Energy (MJ)	GHGs (CO_2 eq.)	Total Energy (MJ)	Fossil Energy (MJ)	GHGs (CO_2 eq.)
Nitrogen fertilizer	384.0	379.0	23695.9	418.6	413.1	25825.3
Phosphorous fertilizer	17.0	16.3	1251.4	38.7	37.0	2846.6
potassium fertilizer	10.7	9.9	826.4	24.3	22.4	1879.8
Herbicide	129.1	123.2	9932.6	51.4	49.1	3956.1
Insecticide	102.6	97.7	7770.1	23.7	22.6	1793.6
Land emissions	0.0	0.0	35494.3	0.0	0.0	38683.9
Diesel	30.5	29.9	3006.5	52.1	51.0	5132.9
Seed	0.0	0.0	0.0	21.0	20.5	2762.7

Figures

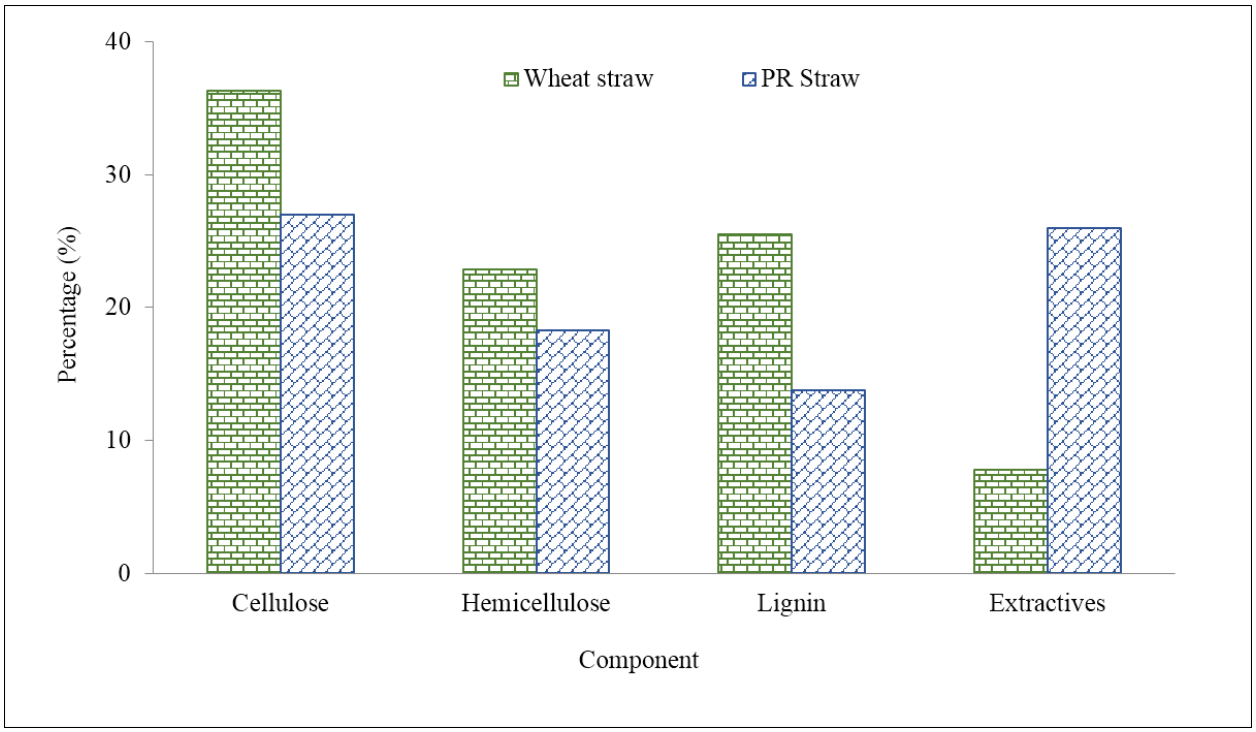

Figure 1 Chemical composition of perennial ryegrass straw and wheat straw on dry basis

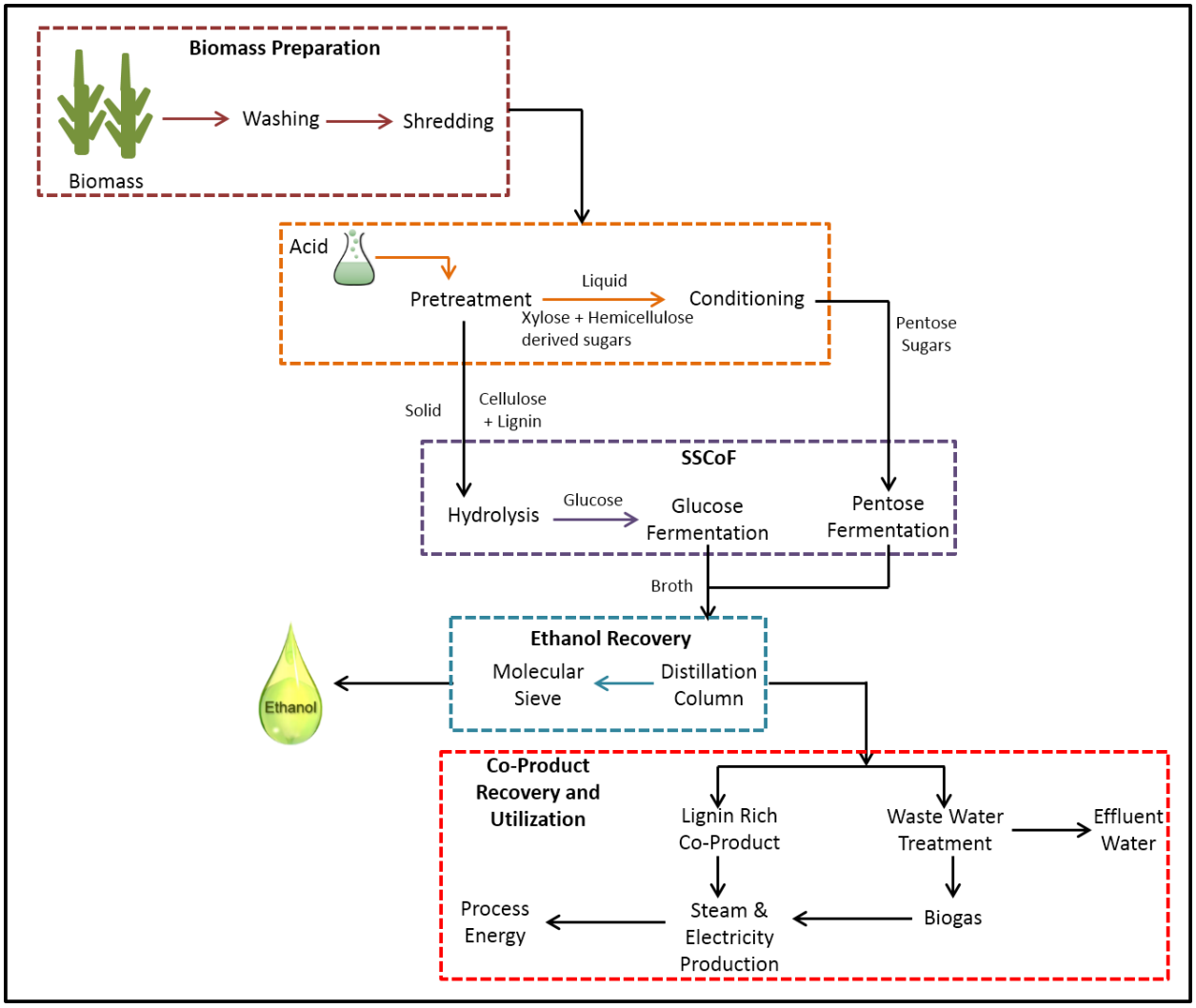

Figure 2 Schematic illustration of modeled ethanol production process

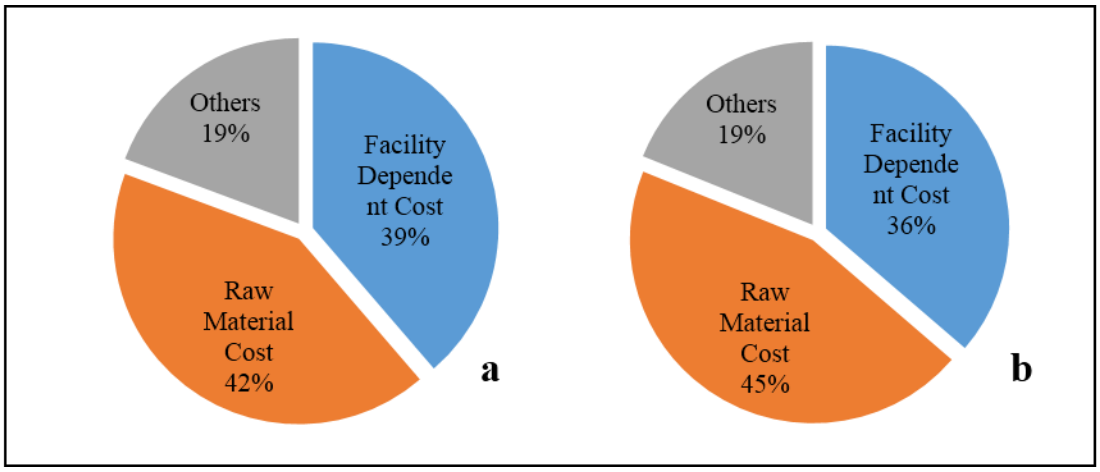

Figure 3 Contribution of facility dependent, raw material and other costs in total operating cost during ethanol production from (a) PR straw (b) wheat straw

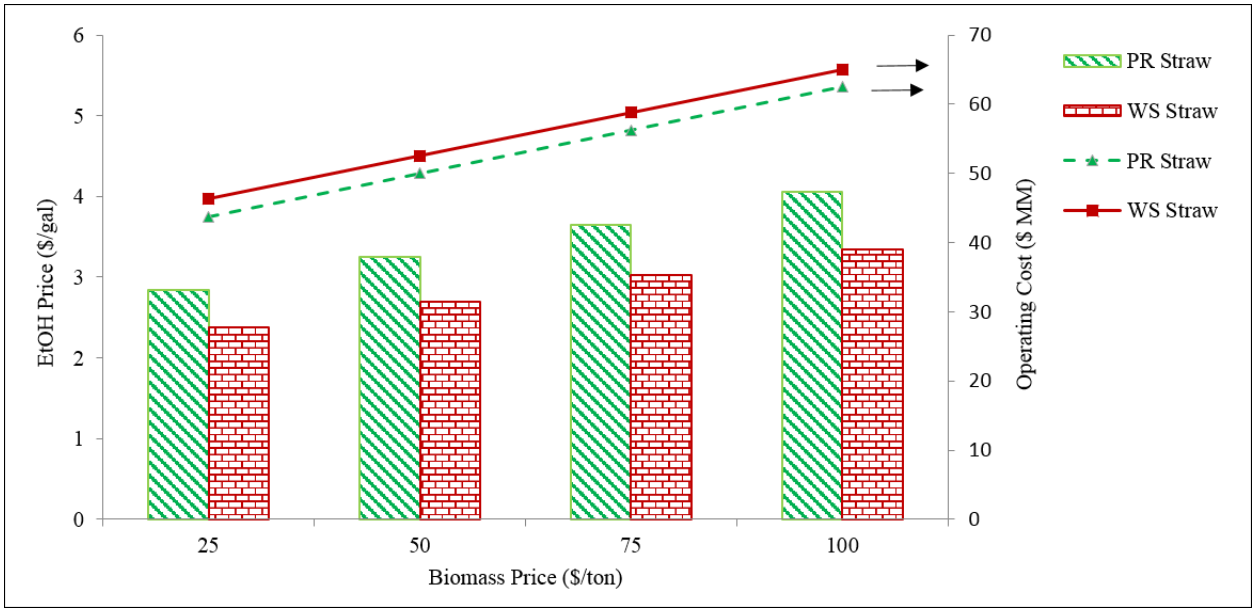

Figure 4 Effect of biomass price on cost of ethanol produced from PR and wheat straw

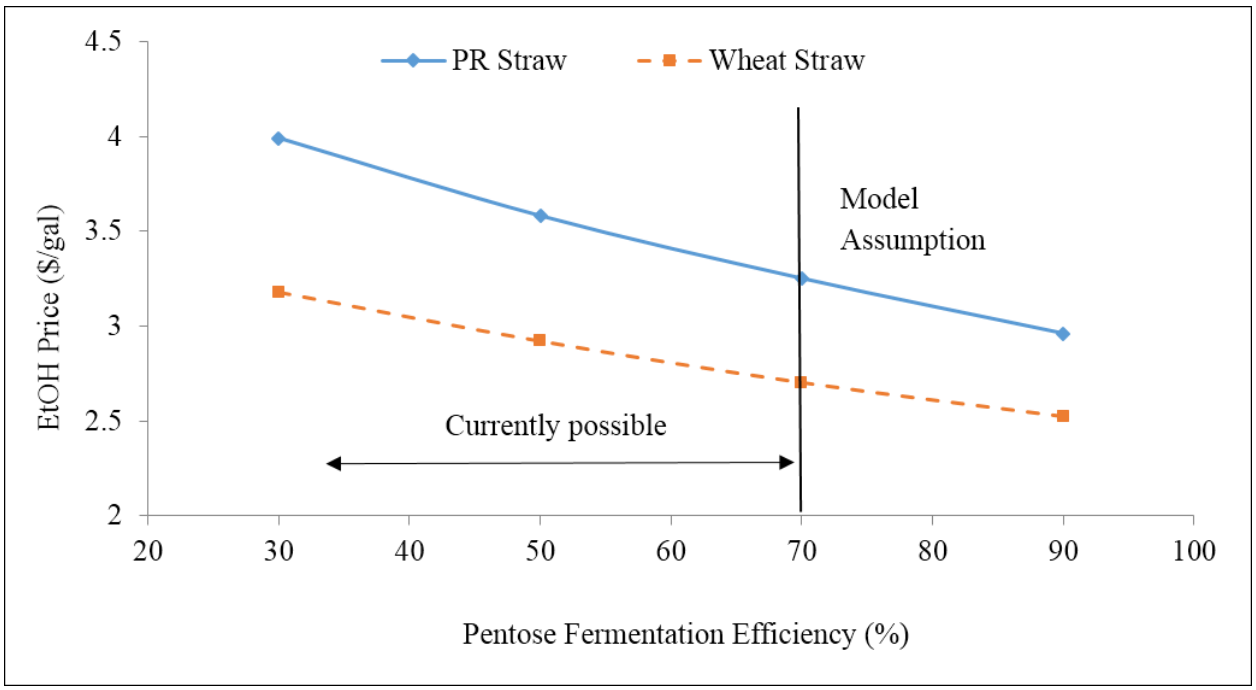

Figure 5 Effect of pentose fermentation efficiency on price of ethanol produced from PR and wheat straw

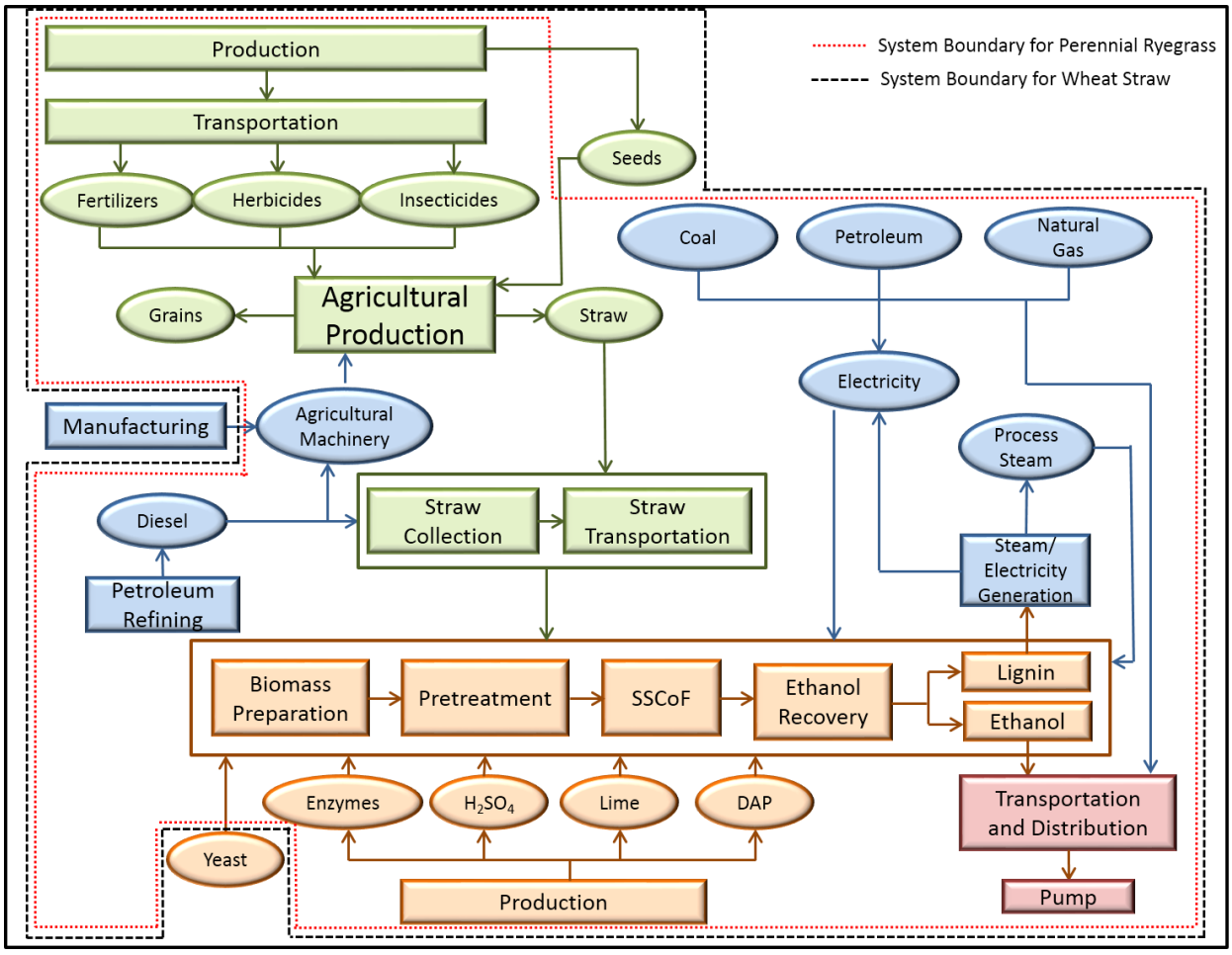

Figure 6 System Boundary for life cycle analysis of ethanol production from PR and wheat straw

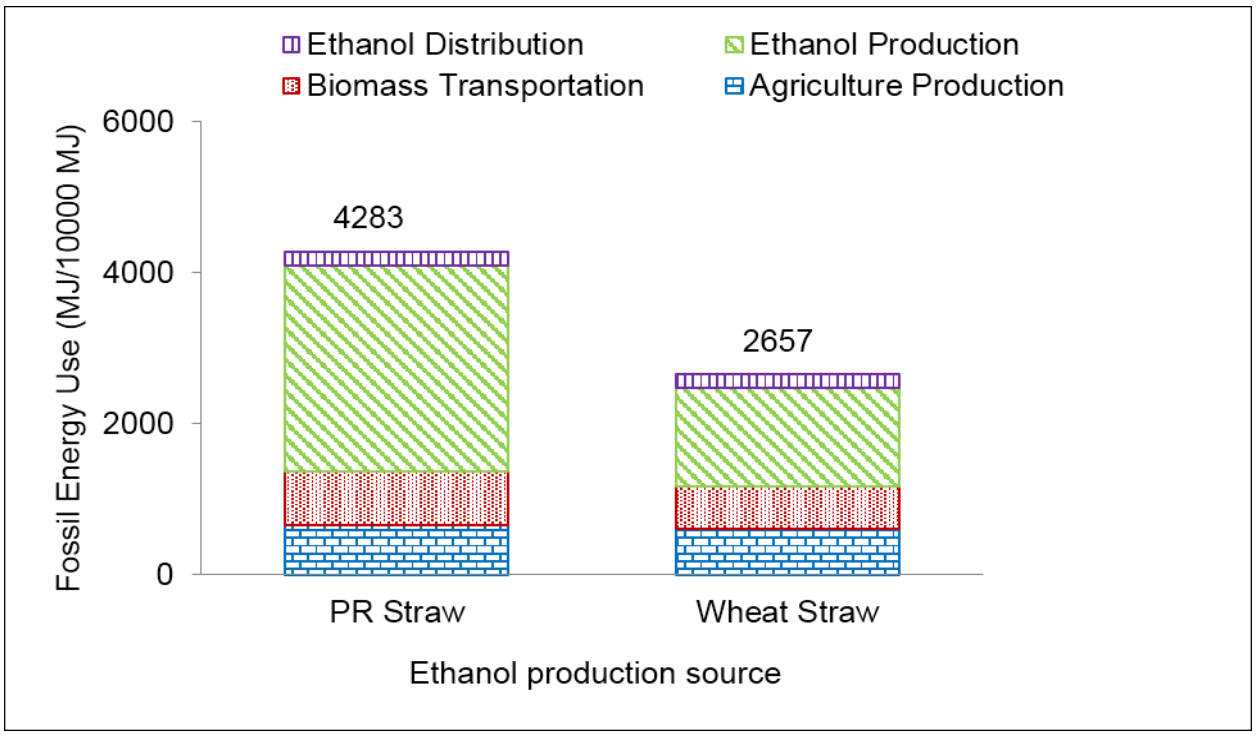

Figure 7 Fossil energy used to produce 10,000 MJ ethanol energy during various stages of life cycle of ethanol

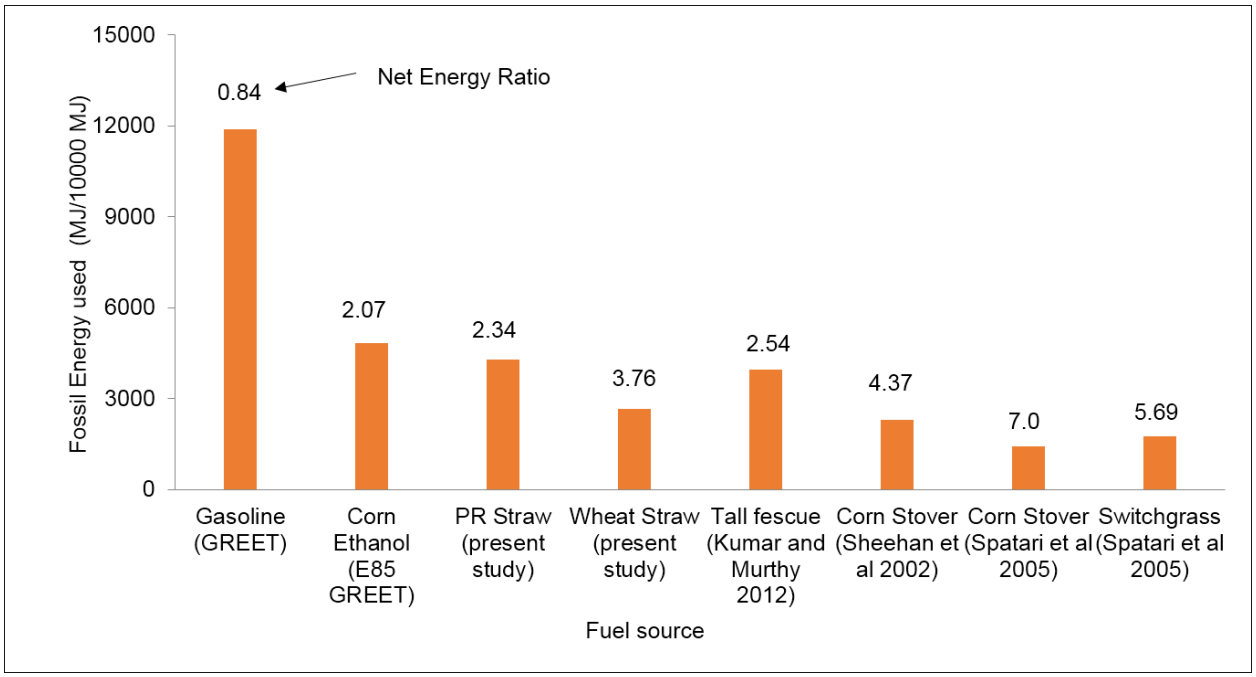

Figure 8 Comparison of fossil energy used to produce 10000 MJ of fuel energy for various fuels and fuel sources

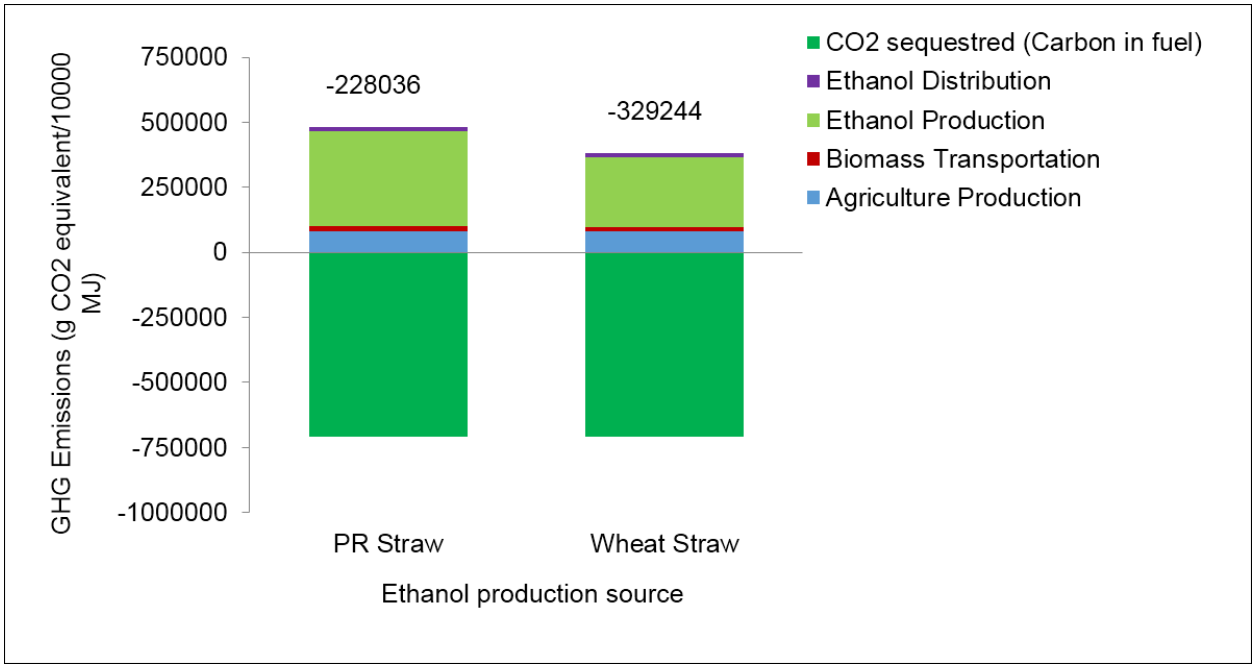

Figure 9 GHG emissions produced per functional unit (10,000 MJ ethanol energy) during various stages of life cycle of ethanol

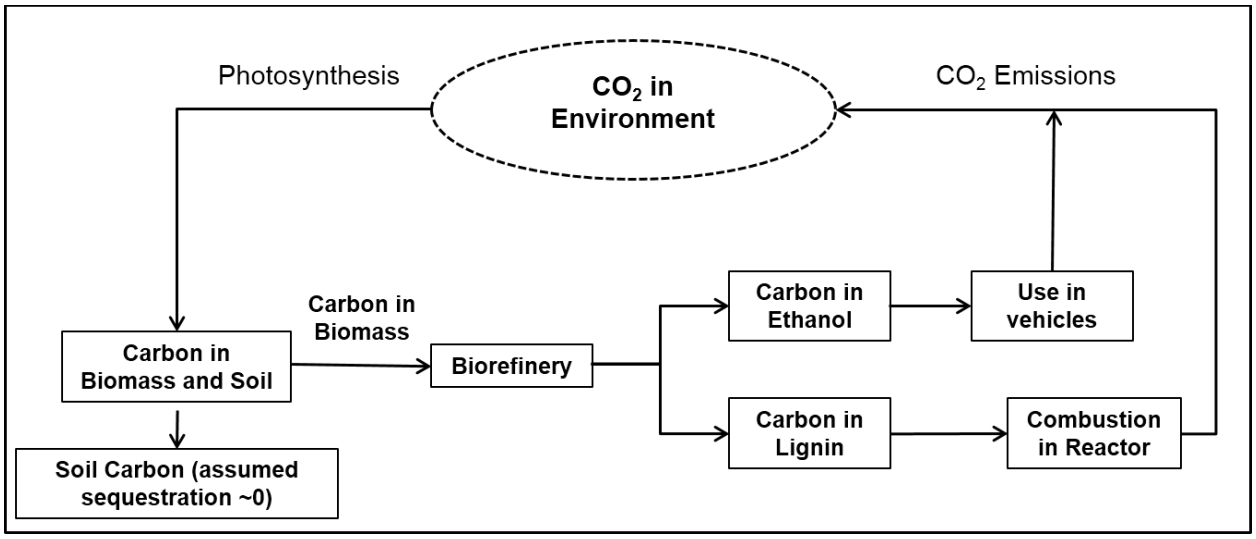

Figure10 Carbon balance during life cycle of ethanol production

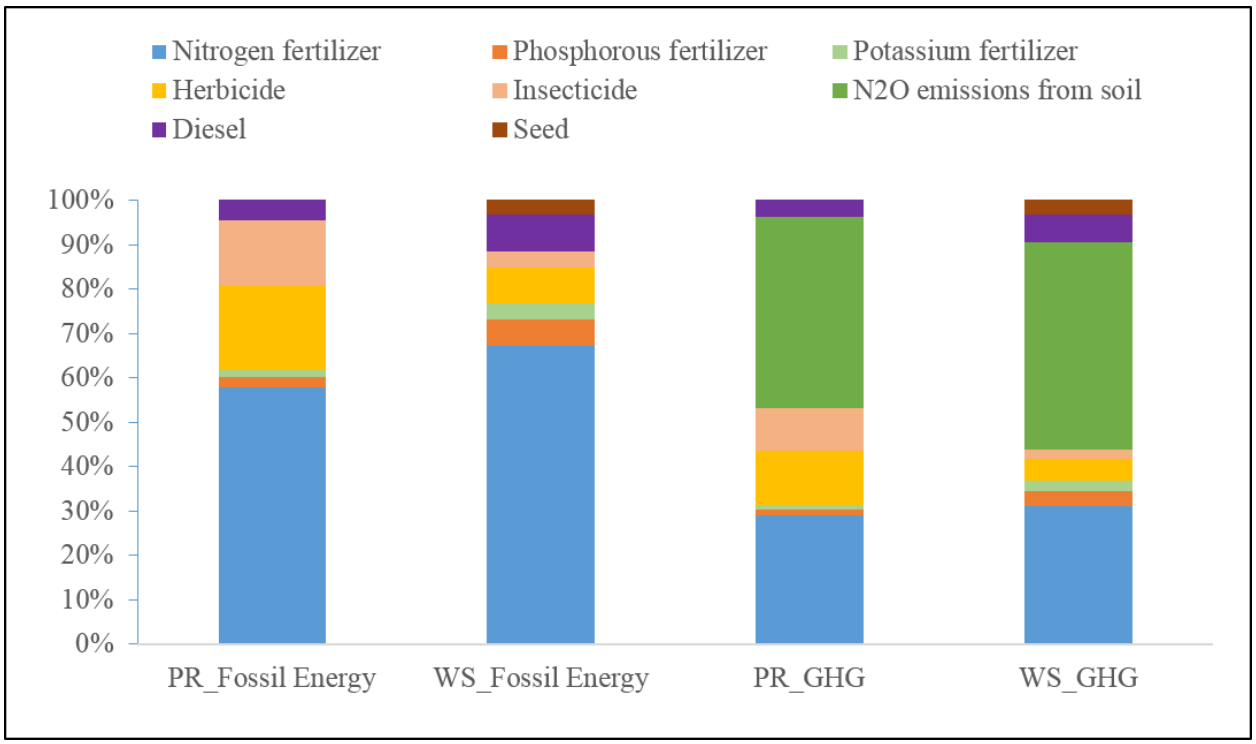

Figure 11 Percent contribution of various inputs during agricultural production (WS: Wheat Straw)

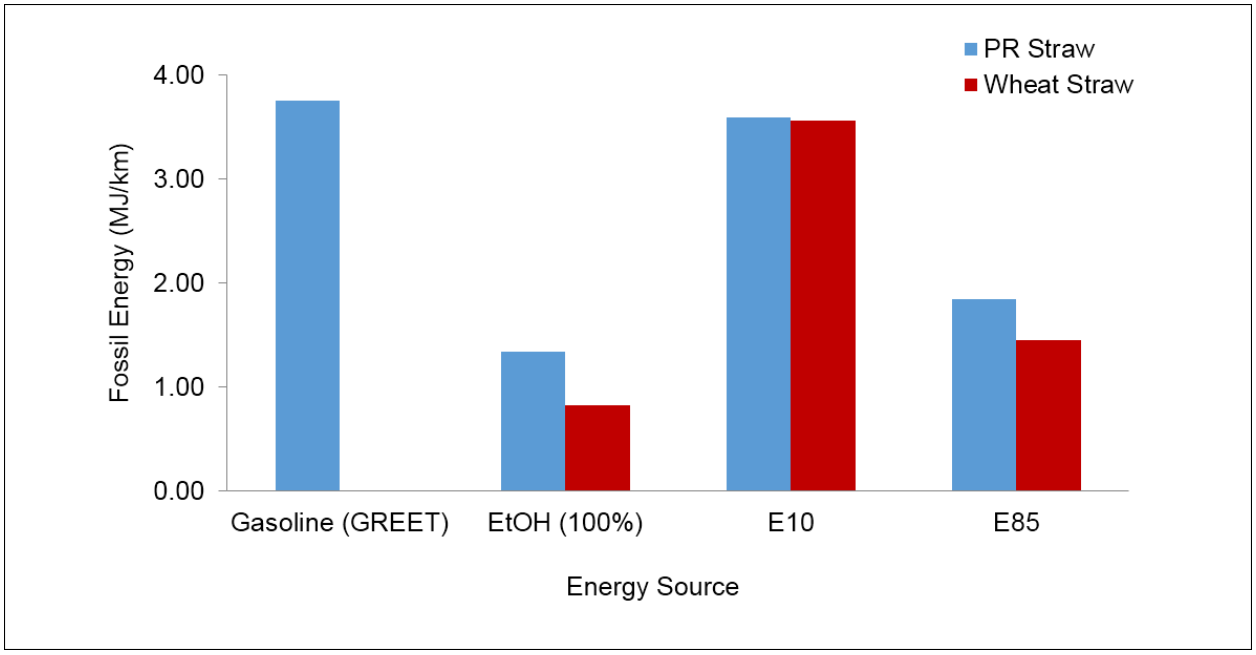

Figure 12 Fossil energy used during life cycles of different fuel blends required for 1 km driving