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Article

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Optimization of Surfactant Addition in Cellulosic Ethanol Process Using Integrated Techno-Economic and Life Cycle Assessment for Bioprocess Design

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Abstract

Surfactants have been demonstrated to be effective in increasing the cellulase enzyme efficacy and overall enzymatic hydrolysis efficiency. However, the impact of the surfactant addition on the economic viability and environmental impacts of the bioethanol process has not been well investigated. The objective of this study was to determine the economic and the environmental impacts of using five surfactant types, Polyethylene glycol (PEG) 3000, PEG 4000, PEG 6000, PEG 8000 and Tween 80, at various concentrations (8, 5, 2, 1, 0.75, 0.5, 0.25 and 0 % w/w) during enzymatic hydrolysis and fermentation of pretreated Banagrass. We used an integrated techno-economic and life cycle assesment to guide the selection of optimal surfactant concentration in the bioethanol process. Surfactants concentration of more than 2% negatively affects the profitability of ethanol even when there is a statistically significant increase in glucose and ethanol titers. Based on the overall performance indicators for final ethanol, economic viability and environmental impacts, the addition of PEG6000 at 2% (w/w) were determined to be the optimal option. Glucose and ethanol concentrations of 119.2±5.4 g/L and 55.0±5.8 g/L respectively with 81.5% cellulose conversion rate were observed for 2% (w/w) PEG6000. Techno-economic and Lifecycle analysis indicated that 2% w/w PEG6000 addition resulted in ROI of 3.29% and had reduced the global warming potential by 6 g CO2/MJ ethanol produced.

Keywords: process design, techno-economic analysis, sustainable processes, life cycle assessments, biofuels, hydrolysis, fermentation, lignocellulose

Introduction

While every unit operation in the biofuel production processes has an impact on overall commercial viability, the enzymatic hydrolysis process is considered to be a bottleneck in the lignocellulosic bioprocessing[1]. Non-productive binding of the enzyme is one of the challenges that limit enzyme productivity and reduce cellulose hydrolysis[2]. Polyethylene glycol (PEG) has been reported to enhance enzymatic hydrolysis of pretreated lignocellulosic feedstocks increasing hydrolysis and fermentation yields[3-8]. The possible mechanisms for enhancing enzymatic hydrolysis include (1) hydrophobic structure of surfactants form a coating around lignin thus preventing enzymes from adsorbing to lignin; (2) surfactants alter lignocellulose structure and enhance cellulose accessibility; (3) surfactants form reverse micelle that envelope enzymes and protect it from denaturing[3, 9]. While different types of surfactants were investigated[3-8] using different concentrations (0.5% - 5%), these studies were primarily focused on establishing technical feasibility of the process and did not include a systems perspective including the economic and environmental impacts of surfactants addition. Price of PEG, for instance, which varies between $1800-2700/ton[10] depending on the type of the PEG and its addition could have a significant impact on process economics.

Despite many technologies that are successful at the laboratory and pilot scale, many questions regarding their economic viability and environmental impacts are still unanswered and are being investigated[11]. In fact, it is well known in the technology development and commercialization domains for novel technologies that only 1% of initial discovery projects end up as commercial process[11]. It takes between 10-15 years of research to develop product/processes and commercialize. Between 75-95% of the patents filed do not generate

any income through royalties or licensing in industries[12-13]. This is due to various reasons such as policies, incentives, market, environmental threats etc.

There is a critical need for a paradigm that considers technological, economic and environmental impacts from the process of ideation to commercialization[14]. Techno-economic (TEA) and life cycle assessment (LCA) are used to assess the technical feasibility, economic viability and environmental impacts of a process when a technology is in the pilot or large scale. These tools can be employed in a novel way to develop a paradigm that ensures consideration of the above mentioned three factors early in the research cycle to identify bottlenecks to commercialization and lower environmental impacts.

This paper focuses on determining the effect of surfactants on ethanol production in an integrated TEA and LCA framework. The objectives of this work are as follows:

1. Study the effect of various surfactants at various concentrations on ethanol production using lignocelluloses.
2. Assess the economic, and environmental impacts to determine the optimum concentration of the surfactant.

Methods

Materials

Feedstock: Dilute acid pretreated Banagrass (*Pennisetum purpureum*) was obtained from a pilot facility in Boardman, OR. Biomass was washed with 3X water on a weight basis and pH was adjusted to 5.5 using NaOH. After pH adjustments, excess moisture was removed using hand press and air dried until the moisture was 30% (W/W). Composition of biomass and other process streams was determined using NREL protocols[15-17]. The cellulose content of pretreated

biomass was 60.1 % (w/w), and other sugars were <4%. Air dried Banagrass was stored at room temperature until further use in all subsequent experiments.

Chemicals: For the first set of enzymatic hydrolysis experiments, surfactants namely, PEG 3000, PEG 4000, PEG 6000, PEG 8000 and Tween 80 were used at four concentrations (0%, 2%, 5%, and 8%). For the second set of experiments, PEG 6000 was used at five concentrations (0% 0.25%, 0.50%, 0.75% and 1.0%). A commercial cellulase enzyme mixture (Ctec2, Novozymes, USA) was added at the rate of 20 mg protein/g glucan in a single dose[18] at the beginning of the experiments as per the manufacturer's recommendation. *Saccharomyces cerevisiae* (active dry yeast BIO-FERM® XR) was added at the rate of 1.0 g/L to initiate fermentation process. Urea (1.0g/L) was added as nitrogen source for the yeast, while tetracycline (400 µl/L from the stock solution of 5mg in 70% ethanol) was added to limit any bacterial activity[18].

Software: Intelligen SuperPro Designer (V 8.5) was used for simulating and analysing the techno-economic feasibility while Open LCA (V 1.6.3) was used to calculate the environmental impacts. The Ecoinvent database 3.1 was used to collect the inventory for conducting LCA, and TRACI 2.1 was used as an impact assessment method[19-21].

Experimental design and process design tool description

A literature review of various surfactants (PEG 3000, PEG 4000, PEG 6000, PEG 8000, and Tween80) indicated that 5% was optimal for efficient ethanol production[9]. First set of experiments were conducted based on the reported surfactant concentrations mentioned above at 5±3% i.e., (2%, 5% and 8%) using dilute acid pretreated Banagrass. The experiments involved a combination of enzymatic hydrolysis (glucose release) followed by fermentation for ethanol production. All the experiments were conducted in triplicates and a control without any

surfactant was used in all experiments. In total 50 shake flasks (250 ml with a working volume of 100 ml) were used for the first experiments in the combinations of 5 surfactants (PEG 3000, PEG 4000, PEG 6000, PEG8000, and Tween 80) X 3 concentrations (2%, 5% and 8%) X 3 replicates + 5 controls (no surfactant) (S2:TableS2-S1). The enzymatic hydrolysis was carried out for 96h followed by fermentation for 96h with periodic sampling. Enzymatic hydrolysis was performed at 50°C, while fermentation was carried out at 30°C. The overall solids loading for the batch experiments were maintained at 20%. At the beginning of the experiments, 10% of solids were loaded and the remaining 10% was equally split into 3h intervals. Based on the experimental data on glucose and ethanol yield, a statistical analysis was performed using ANOVA-General Model to determine differences in final sugar and ethanol concentrations at various surfactant type and concentrations. Based on the experimental results and the statistical analysis, the selected type and concentrations of surfactant were used in further TEA analysis (described in section 2.3 and 2.4) and LCA analysis (described in section 2.5) to minimize the economic and environmental impacts associated with the surfactant addition. A return on investment (ROI) was used as a parameter to compare the economics and the ROI was noted.

To identify optimum concentration of the best surfactant identified in the first set of experiments described above, a second set of experiments were performed at 0.25%, 0.50%, 0.75% and 1.0% concentrations. The operating conditions including temperatures for enzymatic hydrolysis, fermentation, enzyme loading, solids loading, sampling frequency were same as in first set of experiments, while the overall retention time of the process was reduced to 144h compared to 192h in first experiment. After 72h of hydrolysis, active dry yeast was added to

initiate fermentation. The results from this experiment were input to the process model under same conditions to calculate ROI. The ROI from the first run and as well the second run was compared and analysed. Similarly, the LCA was performed on the best results yielding experiment from the first experiments and all the trials in the second run (lower concentrations). The TEA and LCA results for control experiments (no surfactant) were used as the basis to compare the performance increases and a holistic understanding of the solids loading and the type and concentration of surfactant needed to optimize cost and environmental impacts. Incorporating TEA and LCA iteratively in the early stages of research to identify hotspots will help the researchers to focus on the promising trends for the industries, thus reducing the laboratory to commercialization cycle. An overview of decision-making tool employed in this study is reported in Figure 1.

Model development

The techno-economic model was developed using Intelligen SuperPro Designer (V8.5) based on NREL[1, 18, 22-23]. All the models are attached as supplementary files (S1) to enhance transparency and enable replication of the reported results. Banagrass produced in experimental field plots in Maui, Hawaii was field dried and transported to the facility where it was stored in super sacks for 10-30 days before further processing (S2:Figure S2-S1). The feedstock was washed with recycled water to remove any dirt and ground using a knife mill. Banagrass was pretreated with dil. sulfuric acid 0.75% (W/W) at 158°C and 0.55 MPa with a residence time of 10 min. Subsequently, the slurry was centrifuged to fractionate solid and liquids, where the solid fraction rich in celluloses was washed with 3X water and pH adjusted between 5.0 and 6.0 prior to enzymatic hydrolysis [24-25]. On the other hand, the liquid fraction containing hemicelluloses

and dissolved solids was detoxified by addition of $Ca(OH)_2$and adjusted to 6.00 pH. The calcium sulphate (gypsum) precipitating as a byproduct was recovered using hydrocylones and vacuum filtration.

After gypsum separation, the liquid and solid streams were combined, and cellulase was added at the manufacturer recommended rate of 20 mg protein/ g glucan. Surfactants were added at an appropriate concentration based on the treatment simulated. Enzymatic hydrolysis was performed at 50°C, while fermentation was conducted at 30°C. The techno-economic analysis was based on a retention time of 72 hr for enzymatic hydrolysis process and 48 hr for fermentation (120 hrs total). . The glucose, ethanol yield and conversion rates of different trials used were reported in S2:TableS2-S2. Once enzymatic hydrolysis is complete, yeast and diammonium phosphate (nitrogen source) were added to the process. Separate hydrolysis and fermentation (SHF) was employed as the process configuration for all trials. Ethanol was recovered using in three distillation columns (Feed concentration to 93% ethanol), followed by dehydration in molecular sieves (93% to 99.5% anhydrous ethanol) to remove residual moisture[18]. Ethanol is denatured using 1% gasoline and sold as the main product. The lignin residues from the bottoms of the distillation columns are used in the boiler for steam generation and subsequently electricity production. The boiler operates at 10% excess oxygen where steam is produced at 257°C and 4.5MPa[26].The flue gas exits the boiler at 200°C and steam expansion results in electricity production. The wastewaters from different sources are treated using different technologies including anaerobic digestion, aerobic oxidation and belt filtration.

Economic analysis and assumptions

The plant was designed to process 60,000 dry MT Banagrass/year based on the available land to produce the feedstock on Maui Island. The plant has a lifetime of 20 years with an annual operational time of 7920h. The list of economic assumptions used in this study is tabulated in Table2. Discount rate for the project was 4%, and corporate taxes were maintained with federal standards at 40%. The price of the utilities was based on the previous literatures[1, 18, 27]. The construction period of the plant was assumed 24 months with a start-up time of six months.

Life cycle assessments

Goal, scope, system boundaries and allocation procedure

The primary goal for the LCA was to conduct a cradle-to-gate life cycle inventory and estimate environmental impacts based on the experimental results to determine the process path with lowest environmental impacts. One MJ Ethanol was used as a functional unit in this study. The LCA system boundary (Figure S2-S2) includes farming practices including fertilizers, agricultural machinery, electricity, harvest, water, and transportation as a part of the Banagrass production. Coproducts such as electricity and gypsum were considered avoided products. System expansion was used to avoid allocation and co-products considerations as per the ISO 14044 (2006) standards[28].

Life cycle inventory

The data for the life cycle inventory such as process throughput information including raw material consumption and product yields were obtained from the TEA models. Yeast production process was added separately based on Dunn et al[29]. Feedstock production details such as irrigation data, harvesting, emissions and crop yield were obtained from pilot trials

conducted in Hawaii. All these data were integrated and analysed using Ecoinvent 3.1 database and life cycle impact assessment was conducted on these integrated processes.

Life cycle impact assessment

TRACI 2.1 [30] was used to evaluate LCIA that includes seven environmental indicators including acidification, ecotoxicity, eutrophication, global warming, ozone depletion, photochemical ozone formation (POF), resource depletion – fossil fuels, while the remaining three are human health-related including carcinogenics, noncarcinogenics and respiratory effects. The summary of all process inputs and outputs can be accessed from the supplementary files (S1) using Open LCA with Ecoinvent 3.1 database.

Sensitivity analysis

Since the approach adopted in this work requires use of early stage TEA which often require estimation of estimated parameters due to limited information a detailed sensitivity analysis was conducted to identify the process parameters that have the greatest impact on the TEA results. Impact of ±20% variations in parameters such as ethanol price, capacity, enzyme amount and price, feedstock price, surfactant price on the overall TEA results were assessed. Sensitivity analysis for LCA results was conducted using a Monte-Carlo simulation method consisting of 100 independently sampled runs in OpenLCA software.

Results and Discussion

Effect of surfactants on enzymatic hydrolysis and ethanol production

Pretreated biomass at a solid loading of 20% was used to investigate the effect of surfactants at four concentrations 0% (control), 2%, 5% and 8% (w surfactant /w biomass). The statistical

analysis using ANOVA-General model did not show a significant difference in glucose concentrations for different types of surfactant (P-value >0.05) but there was a significant differences (P-value <0.05) between different concentrations of surfactants for the glucose release (S3). These results indicate that while the addition of surfactant has a positive effect on the glucose release, the results are insensitive to the type of the PEG surfactant used (S4).

After 96h of enzymatic hydrolysis at a level of 2% surfactant, the glucose concentration was 119.2±5.4 g/L for PEG 6000 which was 22.6% higher compared to the control. At a level of 5% surfactant, the highest glucose concentration was 126.9±1.9 g/L using PEG 8000 and represented a 0.06 % increase compared to 2% PEG 6000 results. Similarly, Tween 80 had a glucose concentration of 127.1±5.2 g/L at 8% surfactant and was 0.07 % higher compared to 2% of PEG 6000 (FigureS2-S3). It was obvious that it would not be profitable to use a surfactant >2% as the increase in glucose revenues are less than the additional surfactant price (S2:FigureS2-S6).

Ethanol produced from fermentation followed a similar trend. Ethanol concentrations significantly increased (P<0.05) with an increase in the concentration of surfactant. Like the glucose concentrations, surfactants type did not show a significant effect (P-value>0.05) on ethanol concentration (S3). In addition, the statistical analysis did not show a significant interaction effect between the surfactant type and surfactant concentration on the resulting ethanol. This result indicates that the performance of the surfactants were not significantly different at similar concentrations. PEG4000 and PEG6000 at 2% had ethanol concentrations of 55.6±3.9 g/L and 55.0±5.8 g/L (Figure 2). Ethanol concentrations were 40% and 39% higher compared to control (39.6±3.4 g/L) using PEG4000 and PEG 6000 indicating that the addition of

surfactant had a positive effect on ethanol production. At a level of 5% surfactant, the ethanol concentration was 57.1±2.7 g/L using PEG6000, which represents a 3.8% increment compared to ethanol concentration at 2% of PEG6000. Ethanol concentration of 57.3±4.6 g/L and 57.1±6.1 g/L were obtained using tween80 and PEG6000 at 8% levels which represents an increment of 4.2% compared to ethanol concentration at 2% of PEG 6000.

Given the results of hydrolysis and fermentation process, the positive effect of surfactants becomes even more enhanced during the fermentation process (40% fermentation enhancement compared to 22.6% hydrolysis enhancement). High glucose concentrations (>50g/L) inhibit yeast activity since the hypertonic environment adversely affects yeast viability[30], and the use of surfactants reduce the inhibitory effect on both hydrolysis and fermentation processes. Polyethylene glycol provides exo-protection for the fermentation yeast, boosts its viability and highly enhances yeast tolerance to toxic components[31]. In addition, polyethylene glycol is an effective bactericide and thus reduces bacterial populations that could compete with yeast for glucose[32].

Though the higher concentration of surfactant yielded higher glucose concentration and ethanol production, using a high concentration of surfactant could be detrimental when used in industrial scale due to its relatively high price ($1500-2300/MT). Therefore, based on the experimental results and the statistical analysis 2% PEG 6000 was selected for the preliminary economic feasibility analysis (S2:FigureS2-S6).

Eriksson, et al. [10] reported an overall conversion of 80%, while this study had a overall conversion rate of 81.5% using 2% PEG6000, and a conversion rate of 84.6 % using 5%

PEG6000. Finally, two of the highest conversion rates of 84.9 and 84.7% were obtained at 8% level of surfactant using Tween80 and PEG6000 respectively. Other studies also reported the conversion rate between 75-87% using different surfactants such as PEG 400 , PEG 1500 ,PEG 3000 , PEG 4000 , PEG 6000 and PEG 8000 using 1%, 2%, and 5 % PEG concentration and were typically conducted at 10% biomass loading compared to 20% in the current study [13, 7].

Preliminary economic feasibility analysis

A preliminary techno-economic analysis was carried out comparing control and PEG 6000 at 2% for ethanol production in a plant with feedstock processing capacity of 60,000 dry MT/year. The overall mass balance and bulk flows are shown in S2: Figure S2-S4. At 19,042 MT/year ethanol, a 2% w/w PEG 6000 addition produced an additional 5000 MT compared to control. While the differences in capital cost between control ($45.5M) and PEG 6000 at 2% ($46.0 M) was $0.5 M, the operational costs were $2.6M higher for PEG 2% w/w and were primarily attributable to the PEG 6000 price. Overall, PEG 6000 at 2% led to an increase in revenues from $14.5 M for control to $19.0 M (Figure 2A). PEG 6000 addition at 2% w/w clearly outperformed control on all profitability indexes including ROI -0.87% (control) and 3.29% (PEG 6000) respectively (Figure 2B). This shows that addition of PEG 6000 could be beneficial for second-generation ethanol production process.

Concentrations higher than 2% of PEG 6000, i.e., 5% and 8% were also included in the preliminary TEA since they have higher ethanol yields. For 5% PEG concentrations, 19,220 MT/year ethanol was produced followed by 19,503 MT/year for 8% PEG concentration (S2: Figure S2-S4). Although more ethanol was produced with increasing PEG concentrations, the operating costs also increased with increasing usage of PEG. Higher OPEX increased production

cost, which in turn reduced the return on investment. Therefore, compared to control, PEG concentrations >2% were not economically profitable. The production cost of control was $1.33/kg for 2% PEG, while PEG concentrations >2% yielded a production cost between $1.34-1.50/kg (Figure 2B). Hence, PEG concentrations >2% were not considered for any further analysis. However, further evidence is needed and explore the possibility of reducing the PEG 6000 addition and achieving higher overall profitability. Therefore, a second set of experiments were conducted to optimize the surfactant concentration.

Optimizing surfactant concentrations

The second set of experiments were performed in the laboratory at reduced concentrations (≤1%) on PEG 6000 to optimize the ethanol production and assess the improvements to overall economic and environmental impacts of the process. Enzymatic hydrolysis and fermentation experiments were performed at four concentrations of PEG 6000 i.e., 0% (control), 0.25%, 0.5%, 0.75% and 1%. It was observed in the first set of experiments that most of the glucose was released in the first 72h. Since a reduction in reaction time will reduce the reactor volume benefitting the CAPEX and OPEX, the fermentation time was reduced from 96hours to 72 hours in the second set of experiments. The peak glucose concentrations ranged between 92.7 – 97.5 g/L depending on the concentration of PEG. The highest glucose release was reached with 1% concentration of PEG 6000 at 97.5±4.9 g/L (S2:FigureS2-S5). After 72h, active dry yeast was added to initiate fermentation for ethanol production. Ethanol production peaked at 72 hours after yeast inoculation, at 40.1 – 42.5 g/L, at various concentrations of PEG. PEG 6000 at 1% had

the highest ethanol production of 42.5 ±1.4 g/L with an increment of 10.1% compared to the control (0 % PEG 6000)

(S2:FigureS2-S5). It was interesting to note that the glucose concentrations at PEG 6000 concentrations <1% were not significant different (one-way ANOVA) but the ethanol concentrations were significantly different compared to control (S3 and S4). Progressive hydrolysis during the fermentation process increases the available glucose concentration in the fermentation broth in addition to the accumulated effect of PEG on the enzymatic hydrolysis process and the fermentation process. However, using two-sample T-test, only PEG6000 1% differs statistically than PEG6000 0% (control) indicating that low PEG concentrations did not enhance the fermentation.

Based on the results of the experiments and the statistical analysis (S2:FigureS2-S6), the profitability of these scenarios was assessed by comparing the techno-economic analysis results for PEG concentrations in the range of 0.0% to 2.0%.

Detailed techno-economic analysis

It was evident from the first round of TEA conducted for higher concentrations (0, 2, 5 and 8%) that PEG at 2% that addition of PEG had a positive effect on economics. To assess the optimality of the 2% PEG 6000 concentration, further TEA was performed for concentrations ≤1% of PEG 6000. The CAPEX for ≤1% of PEG 6000 concentrations was ~$45.5M compared to $46M for 2% PEG (Figure 2A). The OPEX had a similar decreasing trend with the decrease in the PEG concentration. The annual ethanol production increased with the increase in PEG concentration and profitability of the plant was directly proportional to PEG concentration (S2: Figure S2-S4). The ethanol production cost for PEG 6000 concentrations ≤1% varied between $0.99 – 1.06/L

and the production cost decreased with an increase in PEG concentration due to higher revenues from increased ethanol production. The production cost for 2% PEG was $0.88/L, which was $0.11 lower than production cost at 1% PEG. The production cost of other reported studies (without PEG addition) were in the range between $0.6 - 1.2/L, which was comparable to the production costs reported in this study[1, 18, 31-32]. Compared with control ($14.5 M), 1% PEG ($16.3 M) resulted in $1.8 M additional revenue while the operational costs under similar conditions increased by $1.2 M, resulting in $0.6M net revenue increase. The ROI for control 1% and 2% PEG were -0.87%, 0.25% and 3.29% respectively.

Use of 200-1400MT/year of PEG 6000 at various concentrations (0.25-2.0%) for the 60,000 MT biomass/year plant was major contributor to the raw materials prices. (S2:TableS2-S3). The utilities including electricity, cooling water, steam etc. for different scenarios are tabulated in S2:TableS2-S4. Comprehensive mass and energy balance reports including detailed economic and profitability analysis reports reported here can be generated using the model files provided as supplementary files (S1). A part of the high-pressure steam (19.5%) produced in the boiler from lignin and other solids was used in the pretreatment reactor while the rest was utilized for electricity generation through turbines. The net electricity generation after consumption for the control and 2% PEG 6000 was 7166 and 4569 MWh/year, respectively. The differences in steam and electricity production are attributable to the differences in the energy production as the energy consumption in all scenarios was similar. This is a direct result of higher efficiencies of cellulose conversion at higher PEG additions resulting in lower amount of hydrolysis and fermentation residues, which are used as feedstock for the steam boiler.

Life cycle assessments

The mass and energy balance information from the techno-economic analysis including control, 0.25%, 0.50%, 0.75%, 1.0% and 2.0% PEG 6000 were used in life cycle assessments. A decreasing trend was observed for all environmental impacts with the increase in the PEG concentration (S2:FigureS2-S7) and is a result of increased ethanol production with increased PEG addition. Compared to control (-2 gCO_2/MJ), 2% PEG (-8 gCO_2/MJ) had reduced the global warming potential by 6 g/MJ ethanol produced (Table3). PEG 6000 concentrations ≤1% had a GWP between -2 and -4 gCO_2/MJ. GREET reported a GWP of 30.8 gCO2 eq./MJ using corn stover as a substrate for ethanol production[33]. The lower GWP for control could be mainly attributed the larger amount of higher impact electricity mix displaced in Mauii compared to the lower amounts of US continental electricity mix used in GREET. Other studies reported were in the range between 24 and 50 gCO_2/MJ[34-35]. Other environmental impacts including acidification, eutrophication etc. followed a similar trend and 2% PEG had the lowest environmental impacts. These results indicate that 2% PEG was both economically viable and environmentally sustainable.

Analysis of collective data

All the data from the two-experiments performed, techno-economic evaluations and LCA were analyzed to find the best possible combination. The preliminary experiments, which were based on the literature, showed that 2% PEG concentration was the optimal option despite having lower final ethanol concentrations. Using 5% or 8% concentrations worsened the economic feasibility of ethanol production compared to 2% of the surfactant addition demonstrating that

addition of surfactant needs to be optimized for economically optimal results rather than using conditions for higher ethanol titers (8% had highest ethanol concentration). The prefeasibility analysis gave an insight on profitability and served as a basis for designing the second set of experiments to optimize the concentration of PEG. The second set of experiments and the economic analysis indicated that the PEG additions were directly proportional to the economic feasibility until 2% and increasing it further decreased the profitability. Life cycle assessments were also revealed a similar trend and a collective analysis of laboratory, techno-economic and LCA perspectives showed that 2% PEG 6000 is the recommended option.

Sensitivity analysis

The TEA sensitivity on PEG 6000 at 2% concentration showed that ethanol price followed by the plant size were two most significant factors (S2:FigureS2-S8). Using 2% PEG6000 addition as a base case, increasing the ethanol price by 20% increased the ROI to 10.65% compared to 3.78% ROI for base case. Variation of surfactant and enzyme price did not have a significant effect on the ROI. Sensitivity analysis of LCA Datasets (S2: Table 5) was conducted for the 2% PEG case. All inputs to the bioethanol process (Biomass, cellulase enzymes, yeast, phosphate fertilizers, lime, sulphuric acid and water) were assumed to vary according to a normal distribution with a standard deviation equal to 10% of the mean value. The mean value was the same as the 2% PEG scenario described earlier. Monte Carlo analysis indicated that there were large variations (>100% mean value) for all the LCIA metrics indicating the extreme sensitivity of the results to the variation in the inputs to the process.

Conclusion

This study was implemented to determine the economically viable and environmentally lower impactful process for addition various surfactant molecules (PEG 3000, 4000, 6000, 8000 and Tween 80) at various concentrations (0-8%) to enhance enzymatic hydrolysis of pretreated Banagrass for sugar release and subsequently, ethanol production. Of the tested surfactants, PEG 6000 was determined to be the optimal surfactant and economic analysis indicated that PEG addition at 2% concentration was the most optimal option with an ROI of 3.29%. Increasing or decreasing PEG 6000 concentration beyond the 2% adversely impacts the economic feasibility. Environmental impacts including global warming potential, acidification and eutrophication potentials all decreased linearly with addition of PEG 6000 up to 2% concentration. Based on the integrated experimental, techno-economic and life cycle assessments, 2% PEG 6000 addition was found to be technically feasible, economically viable and environmentally less impactful pathway for ethanol production from Banagrass.

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Authors Contribution

Haider Jawad Kadhum, and Karthik Rajendran had equally contributed to this manuscript. They conducted the experiments, performed the techno-economic analysis and life cycle assessment and wrote the manuscript. Ganti S Murthy directed the research, reviewed results, provided

critical feedback, performed LCA sensitivity analysis, helped in data analysis, edited and revised the manuscript. All authors read and approved the final manuscript.

Supporting Information

Supplementary 1 (S1): This SuperPro models and LCA model files can be accessed with the freely available demo version (http://www.intelligen.com/), Ecoinvent database and OpenLCA (http://www.openlca.org/).

Supplementary 2 (S2): This file includes all the schematics, system boundary, glucose, ethanol production, raw material and utilities consumption.

Supplementary 3 (S3): This file contains the statistical analysis used in this work.

Supplementary 4 (S4): All the raw data of this work can be accessed from this excel file.

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List of figures:

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Figure 2. Different economic indexes for various concentration of PEG6000. (A) Investments, operating costs, and revenues in million dollars. (B) Unit production cost in $/kg and Return on investment in percentage.

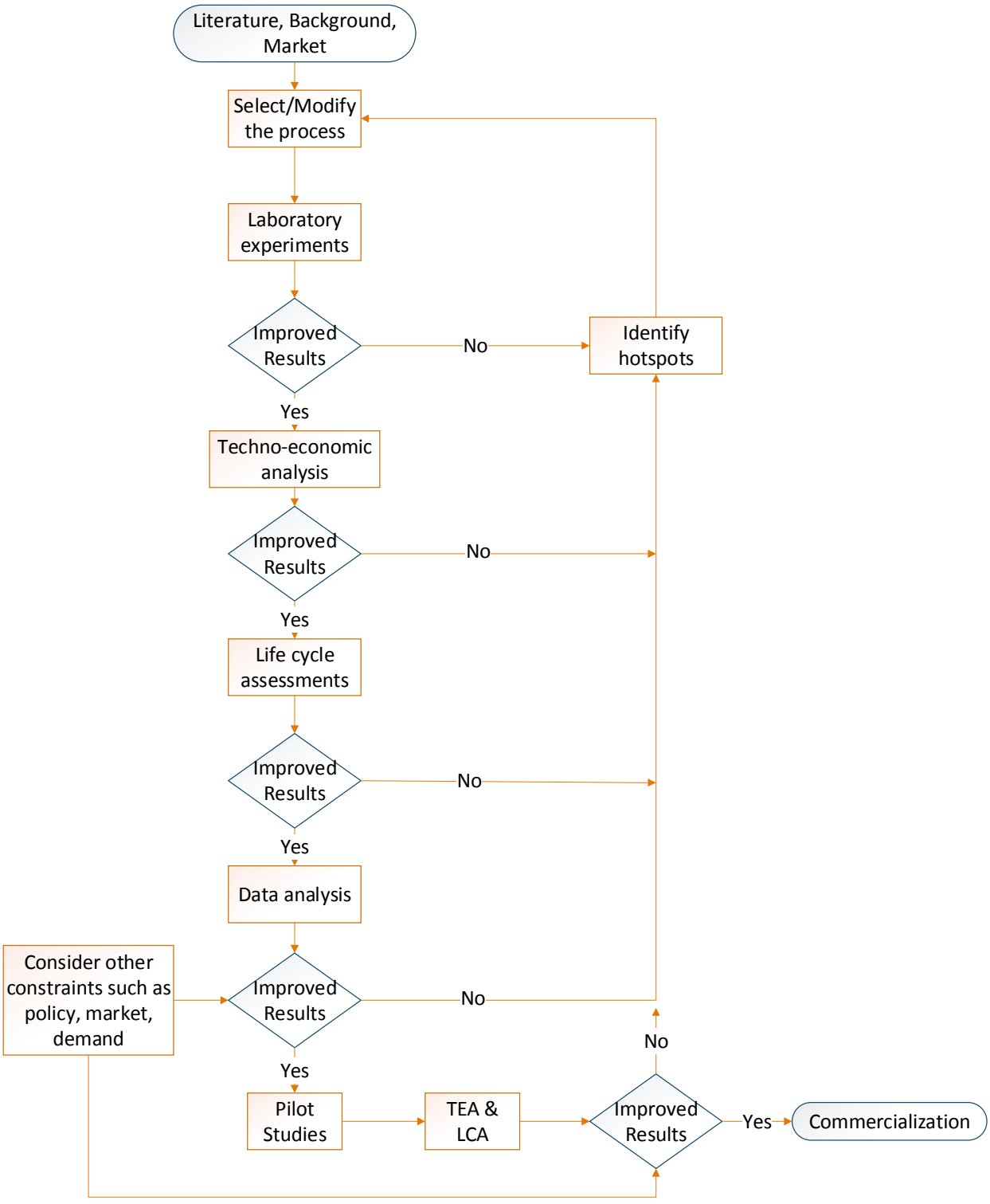


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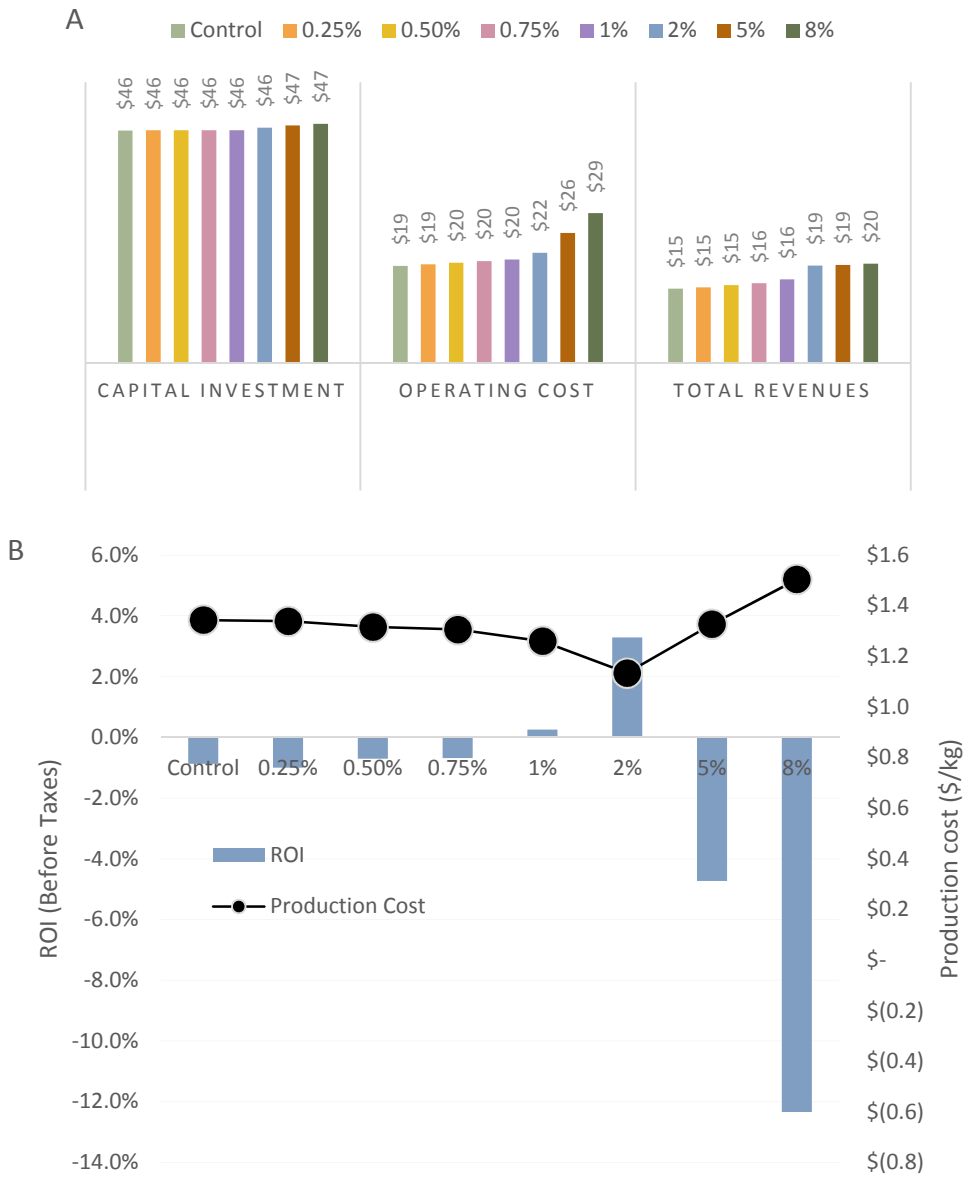


Figure 2. Different economic indexes for various concentration of PEG6000. (A) Investments, operating costs, and revenues in million dollars. (B) Unit production cost in $/kg and Return on investment in percentage.

Table 1. List of assumptions used in this study.

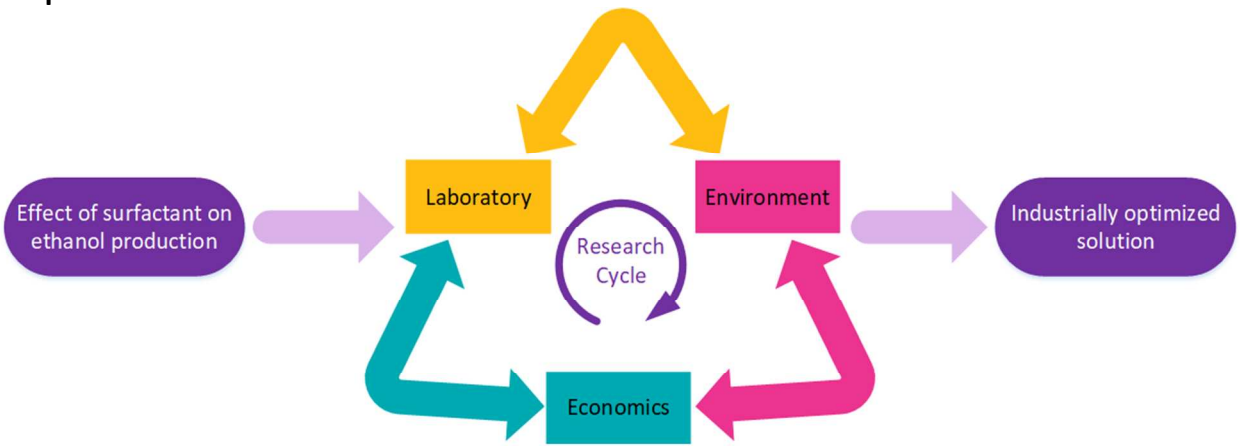
Type	Assumption
Capacity	60,000 dry MT/year
Biomass price	$80/ dry MT
Gypsum price	$30/MT
PEG 6000	$1800/MT
Ethanol price	$0.95/kg
Enzymes price	$0.517/kg
Sulfuric acid price	$35/MT
Electricity price	$0.07/kW-h
Gasoline price	$0.8/kg
Discount rate	4% (2, 4 and 6%)
Annual hours	7920 h
Depreciation method	Straight line
Salvage value	5%
Depreciation years	10 years

Table 2. Overall summary of experimental, techno-economic and life cycle assessments.

			Experimental analysis		Techno-economic analysis				Life cycle assessment									
	Concentration	Surfactant Type	Glucose	Ethanol	Gypsum	Energy	Ethanol	Cost	Acidification	Ecotoxicity	Eutrophication	Global Warming	Carcinogenics	Non-carcinogenics	Ozone Depletion	Photochemical ozone formation	Resource depletion - fossil fuels	Respiratory effects
			(g/L)	(g/L)	MT/yr	MWh/yr	MT/yr	$/kg	kg SO2	CTUe	kg N	kg CO2 eq			kg CFC-11	kg O3	MJ surplus	kg PM2.5
First Experiment	0%	Control	97.24	39.63	3932	7166	14150	$ 1.34	0.00067	0.22107	0.00013	-0.00237	2.03E-09	9.82E-09	1.01E-08	0.005	0.12985	7.56E-05
		Tween80	106.30	51.53														
		PEG3000	107.14	50.96														
	2%	PEG4000	107.31	55.60														
		PEG6000	119.17	54.97	3970	4569	19042	$ 1.13	0.00053	0.18756	1.10E-04	-8.96E-03	1.76E-09	8.32E-09	8.35E-09	4.09E-03	1.19E-01	5.99E-05
		PEG8000	113.42	50.36														
		Tween80	107.32	49.44														
		PEG3000	110.65	49.48														
	5%	PEG4000	116.97	53.86														
		PEG6000	123.89	57.06	3974	4626	19220	$ 1.33										
		PEG8000	126.92	53.92														
		Tween80	127.14	57.29														
		PEG3000	121.21	53.04														
	8%	PEG4000	125.80	56.93														
		PEG6000	118.02	57.10	3978	4342	19503	$ 1.50										
		PEG8000	121.05	53.82														

Second experiment*	0.25%		92.66	40.13	3938	7054	14428	$ 1.34	0.00066	0.22031	0.00013	-2.08E-03	2.03E-09	9.78E-09	9.99E-09	0.00495	1.31E-01	7.47E-05
	0.50%	PEG 6000	89.22	40.81	3944	6822	14920	$ 1.32	0.00064	0.21666	0.00013	-2.54E-03	2.00E-09	9.62E-09	9.77E-09	0.00485	1.30E-01	7.28E-05
	0.75%		92.08	40.68	3949	6657	15277	$ 1.31	0.00063	0.215	0.00013	-0.00259	1.99E-09	9.54E-09	9.63E-09	4.79E-03	0.1299	7.16E-05
	1%		98.69	42.49	3956	6243	16089	$ 1.26	0.00061	2.08E-01	1.20E-04	-4.05E-03	1.93E-09	9.22E-09	9.29E-09	4.61E-03	0.12688	6.86E-05

Graphical Abstract



Synopsis:
A case study of using integrated techno-economic and Life cycle assessments as tools to identify hotspots and optimize bioprocess design