

# Multiobjective Optimization of Biorefineries with Economic and Safety Objectives

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*A new approach for the incorporation of safety criteria into the selection, location, and sizing of a biorefinery is introduced. In addition to the techno-economic factors, risk metrics are used in the decision-making process by considering the cumulative risk associated with key stages of the life cycle of a biorefinery that includes biomass storage and transportation, process conversion into biofuels or bioproducts, and product storage. The fixed cost of the process along with the operating costs for transportation and processing as well as the value of the product are included. An optimization formulation is developed based on a superstructure that embeds potential supply chains of interest. The optimization program establishes the tradeoffs between cost and safety issues in the form of Pareto curves. A case study on bio-hydrogen production is solved to illustrate the merits of the proposed approach. © 2013 American Institute of Chemical Engineers AIChE J, 59: 2427–2434, 2013*

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## Introduction

Recently, the use of biomass as feedstock has gained much attention because of the dwindling fossil-fuel resources and the increasing attention to the climate-change problems. In this context, the concept of a biorefinery is a key ingredient toward sustainability. A biorefinery is an industrial process that converts biomass feedstocks into value-added products such as fuels and chemicals.<sup>1</sup> There are numerous feedstocks and technologies involved in biorefineries. For reviews of these feedstocks and technologies, the readers are referred to literature sources.<sup>2–8</sup> The synthesis and selection of biorefining pathways based on economic performance has been

tackled through optimization approaches. In this context, Pham and El-Halwagi<sup>9</sup> and Ponce-Ortega et al.<sup>10</sup> proposed systematic approaches for the optimal pathway optimization for biorefineries, Bao et al.<sup>11,12</sup> presented techno-economic analysis for the design of integrated biorefineries, Martin and Grossmann<sup>13</sup> and Kokossis<sup>14</sup> presented optimization approaches for synthesizing biorefineries, whereas Tan et al.<sup>15</sup> presented a fuzzy multiobjective approach for the optimization of biorefineries, and Sammons et al.<sup>16</sup> presented an approach for the optimal product allocation in a biorefinery. Furthermore, optimization approaches have been used to develop cost-effective supply chains and site location for biorefineries. For example Bowling et al.<sup>17</sup> implemented a mathematical programming model for the facility location and supply chain optimization of a biorefinery, then Santibañez-Aguilar et al.<sup>18</sup> incorporated simultaneously economic and environmental issues, and You et al.<sup>19</sup> incorporated social

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aspects into the supply chain optimization of biorefineries. Van Dyken et al.<sup>20</sup> proposed a linear programming model for the supply chain optimization of biorefineries, and Dansereau et al.<sup>21</sup> proposed an approach for the sustainable optimization of forest biorefineries. Additionally, Dunnett et al.<sup>22</sup> incorporated scheduling issues in the supply chain optimization of biorefineries, Zamboni et al.<sup>23</sup> incorporated geographical dependence in the supply chain optimization in biorefineries, Eksioglu et al.<sup>24</sup> incorporated operational issues in the supply chain optimization of biorefineries, Dal Mas et al.<sup>25</sup> included uncertainty issues in the biorefineries supply chain optimization, Corsano et al.<sup>26</sup> presented an analysis for the sugar/ethanol system supply chain. The works by Zamboni et al.,<sup>27</sup> Mele et al.,<sup>28</sup> You and Wang,<sup>29</sup> and Elia et al.<sup>30</sup> incorporated environmental aspects in the supply chain optimization of biorefineries.

Notwithstanding the usefulness of the aforementioned approaches, they have focused mostly on economic issues in the selection of the pathways, the design of the process, and the development of the supply chains. Although the economic issues are certainly critical, the important objective of safety has been overlooked or considered as an afterthought following the design. There are significant risks involved in biorefining. Furthermore, the risk assessment should not be limited to the manufacturing site of the biorefinery. Major risks may be involved in the transportation, storage, and processing phases of biorefining. Failure to include the risk involved in the whole supply chain can lead to misleading risk assessment. Indeed, what is needed is a systematic approach to incorporate risk assessment early enough in the design phase of a biorefinery and to account for the risk associated with key life-cycle stages of the supply chain of the biorefinery.

The consideration of risk associated with industrial processes has been the target of recent research.<sup>31</sup> For the specific case of biofuels, several approaches have been reported for the analysis of the risks involved in production. Govasmark et al.<sup>32</sup> presented an analysis for the risk associated to the anaerobic digestion of residues, Law et al.,<sup>33</sup> Pokoo-Aikins et al.,<sup>34</sup> Dinh et al.,<sup>35</sup> and Narayanan et al.<sup>36</sup> presented analysis for the biodiesel production involving technical-economic and risk issues. Li et al.<sup>37</sup> and Riviere and Marlair<sup>38</sup> presented approaches to include safety issues for manufacturing biofuels. Safety metrics have also been included in conjunction with techno-economic criteria for process design and solvent selection.<sup>39–41</sup> Nonetheless, these approaches have exclusively considered industrial processes in isolation of the rest of the supply chain.

Therefore, this article proposes a new approach to explicitly take into account the risks associated with the biorefineries supply chain while incorporating economic factors. Realizing that the objectives of cost and safety may need tradeoffs, we adopt a multiobjective optimization approach to examine the relationship between the two objectives to guide the decision-making process.

## Problem Statement

Consider a biorefinery that converts biomass to biofuel to be used at a certain location. Biomass is transported from several sources with known locations and maximum available supply for each source. Transportation cost is given as a function of the source, flow rate, and distance. The fixed cost of the biorefinery is given as a function of the biomass

flow rate. Risks are associated with biomass transportation, biofuel production, and storage. It is desired to determine the optimal size of the biorefinery based on economic and safety issues.

The following design questions are to be answered:

- How much biomass should be transported from each source?
- How to quantify the risks associated with biomass transportation, biofuel production, and storage?
- How to trade off economic issues (e.g., fixed cost, operating cost, and transportation cost)?
- How to trade off economic and safety objectives?
- What is the optimal capacity of the biorefinery and which intermediates should be made or purchased?

## Proposed Approach

The model representation is based on the superstructure shown in Figure 1. There is a set of industrial facilities (index  $j$ ) that require biofuels or biochemicals (e.g., bio-hydrogen, bio-diesel, bio-ethanol, etc.). To satisfy these requirements, these biofuels/biochemicals may be purchased from an external facility or produced onsite. To produce these biofuels, several feedstocks (index  $i$ ) may be used and processed using given technologies (index  $k$ ). Each supply-chain activity such as harvesting, processing, storage, and transportation has a given unit cost as well as a given risk. It is worth noting that due to the economy of scale the biofuel-production costs tend to be smaller in central external processing facilities, but the associated risk is greater, because in this case it is required the storage and transportation of great amounts of biofuels (which typically pose higher risk than transporting biomass). Therefore, multiobjective optimization is used to establish the cost-risk tradeoffs.

## Model Formulation

Based on the superstructure shown in Figure 1, the general model representation is given in this section.

### Balances for the feedstock

First, the mass flow rate of any feedstock  $i$  ( $F_i$ ) is equal to the sum of the bioresources sent to the central processing facility ( $fc_i$ ) plus the flow rates sent to the industrial facilities  $j$  ( $f_{i,j}$ )

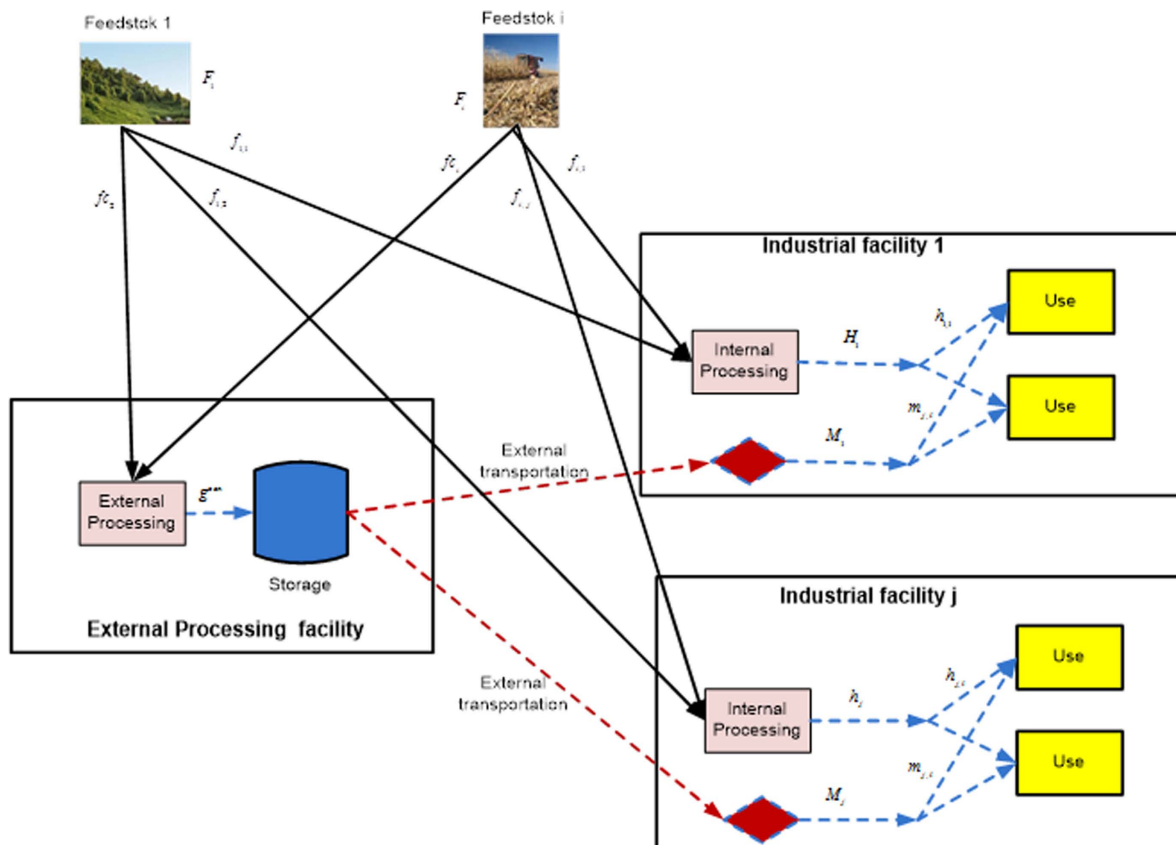
$$F_i = fc_i + \sum_{j \in J} f_{i,j}, \quad \forall i \in I \quad (1)$$

### Balances for the central processing facilities

The central processing facility is modeled considering the optimization for the type of technologies used. This means that there are a set of processing technologies  $k$  for the biofuels production; each technology has associated a given conversion factor ( $\alpha_{i,k}$ ) and the unit processing costs ( $\text{Cost}_k^{\text{Processing}}$ ), as well as the capital costs associated ( $\text{Cost}_k^{\text{Capital}}$ ). This way, the mass balance for the processing facilities is given by the following relationship

$$g^{\text{Cen}} = \sum_{i \in I} fc_{i, \text{ai}} \quad (2)$$

Notice that for each bioresource  $i$  there is an adequate processing technology able to convert the biomass to biofuels with a given conversion factor ( $\alpha_i$ ) and unit processing



**Figure 1. Superstructure for the supply chain of a biorefining system involving economic and risk issues.**

[Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

cost ( $\text{Cost}_i^{\text{Cen\_processing}}$ ); therefore, the associated cost for processing the biomass in the central facilities is given by the following relationship

$$\text{TCost}^{\text{Cen\_processing}} = H_Y \sum_{i \in I} \text{fc}_i \text{Cost}_i^{\text{Cen\_processing}} \quad (3)$$

To determine the capital costs for the processing technologies in the central facilities, the following disjunction is applied

$$\left[ \begin{array}{l} Y_i^{\text{Cen}} \\ \delta_i^{\text{Cen\_min}} \leq \text{fc}_i \leq \delta_i^{\text{Cen\_max}} \\ \text{Cost}_i^{\text{Cen\_cap}} = a_i^{\text{Cen}} + b_i^{\text{Cen}} \text{fc}_i \end{array} \right] \vee \left[ \begin{array}{l} \neg Y_i^{\text{Cen}} \\ \text{fc}_i = 0 \\ \text{Cost}_i^{\text{Cen\_cap}} = 0 \end{array} \right], \quad \forall i \in I$$

This means that the capital costs for the technology to process bioresource  $i$  in the central processing facility is only applied when the flow rate treated is greater than zero. This way, when the Boolean variable  $Y_i^{\text{Cen}}$  is true, then the limits  $\delta_i^{\text{Cen\_min}}$  and  $\delta_i^{\text{Cen\_max}}$  for  $\text{fc}_i$  apply and the associated capital cost ( $\text{Cost}_i^{\text{Cen\_cap}}$ ) is calculated accordingly; on the other hand, when the Boolean variable  $Y_i^{\text{Cen}}$  is false, it means that the flow rate processed is zero and the associated capital cost is zero. This disjunction is modeled as follows

$$\delta_i^{\text{Cen\_min}} y_i^{\text{Cen}} \leq \text{fc}_i \leq \delta_i^{\text{Cen\_max}} y_i^{\text{Cen}}, \quad \forall i \in I \quad (4)$$

$$\text{Cost}_i^{\text{Cen\_cap}} = a_i^{\text{Cen}} y_i^{\text{Cen}} + b_i^{\text{Cen}} \text{fc}_i, \quad \forall i \in I \quad (5)$$

In these equations  $y_i^{\text{Cen}}$  is a binary variable associated with the Boolean variable  $Y_i^{\text{Cen}}$ , such that when the Boolean variable is true, the corresponding binary variable is one and Eqs. 4 and 5 apply, and when the Boolean variable is false,

the corresponding binary variable is zero and the terms  $\text{fc}_i$  and  $\text{Cost}_i^{\text{Cen\_cap}}$  are set to zero.

#### Balances for the feedstock in the industrial facilities

The biofuels produced in each industrial facility  $j$  is obtained by the processing of the bioresources sent to the facility ( $f_{i,j}$ ) times the associated conversion factor ( $\alpha_i$ )

$$H_j = \sum_{i \in I} f_{i,j} \alpha_i, \quad \forall j \in J \quad (6)$$

The operational cost for the biomass processing in the industrial facility is given by the following relationship

$$\text{TCost}_j^{\text{Processing}} = H_Y \sum_{i \in I} f_{i,j} \text{Cost}_i^{\text{Processing}}, \quad \forall j \in J \quad (7)$$

Notice that the operational cost for the industrial facility is different from the one in the central processing facility.

Similar to the central processing facility, the capital cost for the processing facilities is given by the following disjunction

$$\left[ \begin{array}{l} Y_{i,j} \\ \delta_i^{\text{min}} \leq f_{i,j} \leq \delta_i^{\text{max}} \\ \text{Cost}_{i,j}^{\text{Cap}} = a_{i,j} + b_{i,j} f_{i,j} \end{array} \right] \vee \left[ \begin{array}{l} \neg Y_{i,j} \\ f_{i,j} = 0 \\ \text{Cost}_{i,j}^{\text{Cap}} = 0 \end{array} \right], \quad \forall i \in I, j \in J$$

The explanation for this disjunction is similar to the previous one, and the reformulation is stated as follows

$$\delta_i^{\text{min}} y_{i,j} \leq f_{i,j} \leq \delta_i^{\text{max}} y_{i,j}, \quad \forall i \in I, j \in J \quad (8)$$

$$\text{Cost}_{i,j}^{\text{Cap}} = a_{i,j} y_{i,j} + b_{i,j} f_{i,j}, \quad \forall i \in I, j \in J \quad (9)$$

### Mass balances for the users of biofuels

First the total biofuel processed in the central facility ( $g^{\text{Cen}}$ ) is segregated and sent to the participating industrial plants ( $M_j$ ) as follows

$$g^{\text{Cen}} = \sum_{j \in J} M_j \quad (10)$$

In the same way, the produced biofuels in the industrial facilities ( $H_j$ ) can be segregated and sent to the user in the same industry ( $h_{j,l}$ ) as follows

$$H_j = \sum_{l \in L} h_{j,l}, \quad \forall j \in J \quad (11)$$

The users in the industrial facilities ( $W_{j,l}$ ) can obtain the biofuels from the production in the same industry ( $h_{j,l}$ ) and/or from production in the central processing facility ( $m_{j,l}$ )

$$W_{j,l} = h_{j,l} + m_{j,l}, \quad \forall j \in J, l \in L \quad (12)$$

### Economic objective function

The economic objective function considers the minimization of the total annual cost involving the associated cost to the purchase of feedstock, transportation of feedstock, processing in the central facilities, transportation of the biofuels from the central facility to the users, processing costs for the biofuels in the industrial facilities, and the capital costs for the biofuels production for the central facility and users

$$\begin{aligned} \text{TAC} = & H_Y \sum_{i \in I} \text{Cost}_i^{\text{Biomass}} F_i + H_Y \sum_{i \in I} \text{Cost}_i^{\text{Transp-Cen}} f_{c,i} + H_Y \sum_{i \in I} \sum_{j \in J} \text{Cost}_{i,j}^{\text{Transp}} f_{i,j} \\ & + H_Y \sum_{j \in J} \text{Cost}_j^{\text{Trans-biofuels}} M_j + \text{TCost}^{\text{Cen-processing}} + \text{TCost}_j^{\text{Processing}} \\ & + K_F \sum_{i \in I} \text{Cost}_i^{\text{Cen-cap}} + K_F \sum_{i \in I} \sum_{j \in J} \text{Cost}_{i,j}^{\text{Cap}} \end{aligned} \quad (13)$$

### Safety objective function

The consideration for the risks is one of the main targets of the proposed optimization approach. Two questions that arise when dealing with optimization are: how well is a company considering the risk of their main product? And how much are they willing to accept as tolerable? Under these

questions the authors are proposing a new approach that relates the number of fatalities per year and the amount of biofuels produced/bought per year. This is done by inputting the consequence analysis results into the Probit equations. Therefore, the safety objective function can be stated as follows

$$\begin{aligned} \text{Risk} = & H_Y \sum_{i \in I} \text{Fatalities}_i^{\text{Biomass}} F_i + H_Y \sum_{i \in I} \text{Fatalities}_i^{\text{Transp-Cen}} f_{c,i} + H_Y \sum_{i \in I} \sum_{j \in J} \text{Fatalities}_{i,j}^{\text{Transp}} f_{i,j} \\ & + H_Y \sum_{j \in J} \text{Fatalities}_j^{\text{Trans-biofuels}} M_j + H_Y \times \text{Fatalities}^{\text{Cen-processing}} g^{\text{Cen}} + H_Y \sum_{j \in J} \text{Fatalities}_j^{\text{Processing}} H_j \end{aligned} \quad (14)$$

where the associated risk (Risk) is the number of fatalities that can be associated with the given process and that takes into account the fatalities associated with the biomass production ( $\text{Fatalities}_i^{\text{Biomass}}$ ), transportation for biomass to central facilities ( $\text{Fatalities}_i^{\text{Transp-Cen}}$ ), biomass transportation of biomass to distributed facilities ( $\text{Fatalities}_{i,j}^{\text{Transp}}$ ), transportation of products from central facilities ( $\text{Fatalities}_j^{\text{Trans-biofuels}}$ ), and distributed treatment facilities ( $\text{Fatalities}^{\text{Cen-processing}}$ ) to the markets and to the processing ( $\text{Fatalities}_j^{\text{Processing}}$ ). Finally, this article proposes a new approach to relate the consequence modeling and the production per year. Consequence analysis quantifies vulnerable zones for a conceived incident and once the vulnerable zones are identified for an incident, measures can be proposed to eliminate damage to the plant and potential injury to personnel. To determine the number of fatalities, the Probit approach can be used, which can be easily found in the literature.<sup>31</sup> A Probit function is the quantile function (i.e., points taken at regular intervals from the cumulative distribution function of a random variable). This is the inverse cumulative distribution function associated with the standard normal distribution. Probit functions are used in a quantitative risk analysis to predict the number of acute fatalities caused by an accident. A Probit

function describes the lethality rate as a function of any given combination of the exposure concentration and the duration of exposure for a specific substance. An important factor when dealing with flammable substances is the possibility to cause an explosion that could lead to overpressures, which can be estimated using PHAST<sup>42</sup> (software by DNV) or any other workbook.

### Case Study

The case study is based on the hydrogen-production problem taken from Refs. 43 and 44. The process involves several units including gasification to syngas (containing primarily CO, H<sub>2</sub>, CO<sub>2</sub>, hydrocarbons, and other gases such as NH<sub>3</sub> and H<sub>2</sub>S) and tars, steam reforming ( $\text{C}_n\text{H}_m + n\text{H}_2\text{O} = (n + m/2)\text{H}_2 + n\text{CO}$ ) and water-gas shift ( $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ ), gas cleanup and conditioning, and hydrogen separation. First, the input data are presented, and then the computational results and analysis are shown.

### Input data

The following data are mostly adapted with revisions and updates from literature sources<sup>43,44</sup>:



- The hydrogen yield is 70 kg of H<sub>2</sub> produced from the process/tonne dry biomass fed to the process.
- The variable operating costs include: biomass feedstock of \$0.75/kg of produced H<sub>2</sub>, other raw materials of \$0.11/kg of produced H<sub>2</sub>, catalysts of \$0.005/kg of produced H<sub>2</sub>, waste disposal of \$0.03/kg of produced H<sub>2</sub>, and electricity of \$0.08/kg of produced H<sub>2</sub>.
- The first 200 tonne/day of biomass are locally available, and, therefore, the feedstock cost (\$0.75/kg of produced H<sub>2</sub>) includes the transportation cost. Above 200 tonne/day, the biomass will have to be hauled from a long distance. The higher the biomass demand, the larger the cost of transportation per tonne of biomass. For flow rates greater than 200 tonne/day, the transportation cost is given by

Annual transportation cost of biomass (\$/yr) = 0.4 \* (Flow rate of biomass in tonne/day – 200) \* (Flow rate of biomass in tonne/day)(15)

- For practical considerations, an upper-bound constraint on the capacity is taken to be 2000 tonnes biomass/day, which corresponds to the case described by Spath et al.<sup>44</sup>

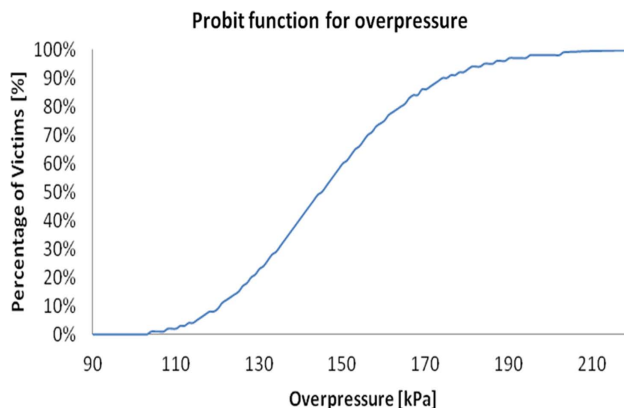
### Computational results

First a break even economic analysis is implemented to project the best capacity of the plant to obtain the minimum selling price of biohydrogen. Suppose that a company is interested in producing hydrogen at a certain location and is interested in determining the optimum size of the hydrogen-producing biorefinery. The decision-making process should consider the economic vs. the safety considerations and should determine whether hydrogen should be made or purchased. If the decision is based solely on economic factors, then the economy of scale favors larger plant sizes, which leads to a facility processing the maximum allowable throughput of 2000 tonnes biomass/day and producing 140 tonnes hydrogen/day. Now, what if the safety issues are considered in the decision making?

### Safety Analysis

Regarding the risk analysis, several factors are to be considered. For the case of hydrogen production (referred to as the “Make” scenario), these include the risks associated with the storage, transportation, and conversion of biomass as well as the storage of the produced hydrogen in a facility. It includes storage of biomass and hydrogen. For the case of purchasing hydrogen (referred to as the “Buy” scenario), the risk factors are associated with the manufacture (including processing and storage of biomass and hydrogen) and transportation of hydrogen. A key difficulty in assessing the risk in manufacturing and storage of hydrogen is assessing the impact of overpressure. Overpressure is the pressure caused by a shock wave over and above normal atmospheric pressure. The shock wave may be caused by sonic boom or by explosion. Blast overpressure is a damaging outcome of explosive detonations and firing of weapons and exposure to blast overpressure shock waves results in injury. Probit functions may be developed to estimate the fatalities vs. overpressure. Figure 2 shows an example of the Probit function.

Hydrogen, being one of the most likely energy sources to be used in the future has a very interesting behavior. It has a very wide flammability limit range (4% lower flammability limit and 75% upper flammability limit); this implies that it

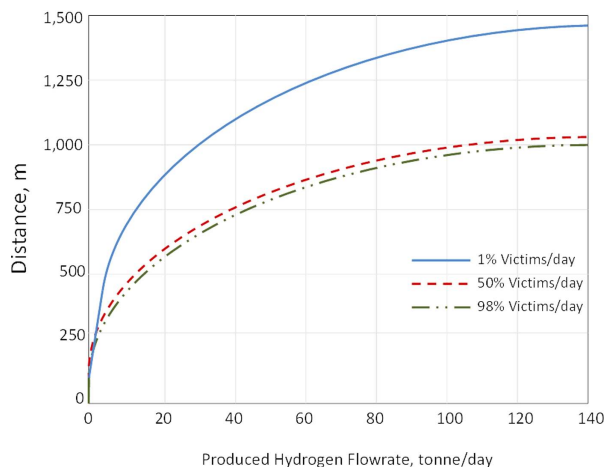


**Figure 2. Probit function for overpressure**  
 $y = -77.1 + 6.91 * \ln(P_s)$ <sup>31</sup>

[Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

is easy to ignite. Furthermore, it requires very low energy to ignite. For instance, when hydrogen is ignited, it does not produce environmentally benign gases, its flame is colorless and there is not soot formation, making a hydrogen fire hard to detect on daylight conditions. Moreover, contrary to natural gas, it presents no difficulty in exploding. A very important characteristic of hydrogen is that it has a high flame speed and if there is an optimal amount of turbulence in the system, a transition from deflagration to detonation (DDT) is very likely to occur. DDT characterizes for resulting in high overpressures and, consequently, massive damages to the surroundings. Currently, some research is being performed to estimate how likely it is for hydrogen explosion to undergo into DDT.<sup>45</sup> This article focuses in the overpressure effects, in terms of fatalities, if a hydrogen explosion occurs using Probit equations. The Probit equations used relate deaths due to a lung hemorrhage to peak overpressure. In this case, Probit equations allow the correlation of the effect of overpressure to percentage of people killed for a certain level of damage. Furthermore, Probit equations correlate directly the percentage of affected population.<sup>46</sup> In addition, only the effects of an explosion on both storage and transport were considered, fire scenario for hydrogen is not being considered. Basically, a hydrogen fire will be more likely to occur when hydrogen is in liquid state. Moreover, if a leak of hydrogen occurs, its evaporation rate will be very high, meaning that a vapor cloud will be formed faster. Furthermore, the effects of radiation are important when a facility siting study is being performed; however, it has been observed that the overpressure affects are by far, more devastating than the radiation effects. This is the main reason why a risk of fire for hydrogen has not been considered in the case study. Furthermore, the risk associated with the fire of biomass is significantly lower than the risk associated with the explosion of hydrogen, and with an adequate storage and transportation system, the risk associated with the fire of biomass can be disregarded.

When hydrogen is made inside the industrial facility, using the Probit function shown in Figure 2 ( $y = -77.1 + 6.91 * \ln(P_s)$ ) and varying the desired amount of hydrogen produced per day, the plots shown in Figure 3 are obtained. These graphs illustrate the estimate fatalities over a range of hydrogen production rate and distance of impact. For the purposes of this article, a series of simulations were made fixing the

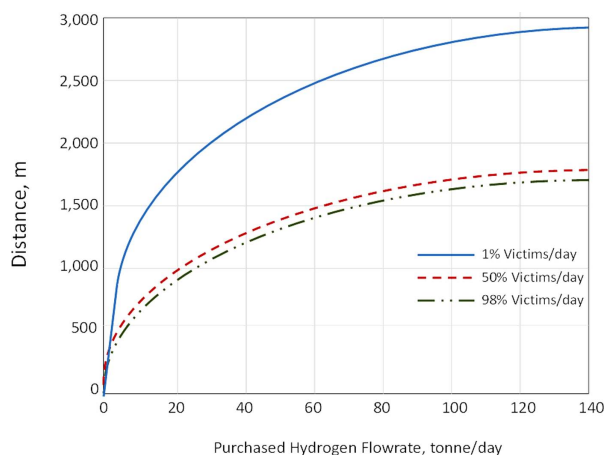


**Figure 3. Fatalities resulting from a hydrogen explosion at different hydrogen production capacities for various distances (for the Make scenario).**

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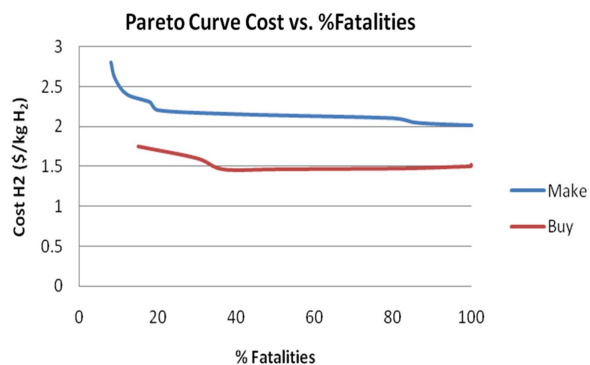
percentages of lethality to 1, 50, and 98%, which correspond to a Probit value of 2.67, 5, and 7.05, respectively. From this and using the equation earlier, one can find that the overpressure for such Probit values corresponds to an absolute pressure of 100,000, 140,000, and 200,000 Pa, respectively.<sup>46</sup> After establishing such values, a series of simulations were performed using PHAST (DNV). From these simulations, overpressure contour effects were obtained for the specified overpressures. These simulations do not consume much timing computing. It is worth noting that higher hydrogen rates lead to greater distances of impact for a certain rate of fatalities. It is also worth mentioning that there is not much difference in the distance of impact for the range of 50–98% fatalities, whereas a major difference is observed for the case of 1% fatalities. This is due to how fast the overpressure decays as the explosion wave moves farther away from the epicenter of the explosion until it reaches a nearly asymptotic behavior.

Now let us consider the case when hydrogen is purchased by the company (the Buy scenario). Working under the same



**Figure 4. Fatalities caused by a hydrogen explosion at different purchased rates.**

[Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 5. Pareto curve for the case study.**

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tools (e.g., Probit function), the same types of graphs are plotted as shown in Figure 4. It is worth observing that a hydrogen explosion in the Buy scenario has higher impact than the Make scenario. This is attributed the cumulative risk of producing and transporting hydrogen in the Buy scenario, which involves higher risk than transporting biomass followed by producing hydrogen in the Make scenario.

The aforementioned risk information is to be used in the optimization formulation to establish the cost-risk tradeoffs.

## Optimization Formulation

The optimization formulation was coded using the software LINGO.<sup>47</sup> The problem consists of 198 continuous variables and 270 constraints. The problems were solved in a computer with an i7 processor at 2.8 GHz with 8 GB of RAM in an average of 0.1 s of CPU time for each point.

Next, a multiobjective optimization approach is implemented to represent the tradeoffs between the considered objectives through Pareto curves. In this case, the solution for the minimum TAC without considering the associated risk yields the solution for the maximum considered risk, and then there is implemented the solutions for the minimum risk without considered the TAC to yield the solution with the maximum associated TAC. Then, the single-objective optimization problem for minimizing the associated TAC is implemented for several constraints of the maximum associated risk in the interval of maximum and minimum risk previously determined. This way, using the multiobjective optimization approach, we obtained the Pareto curve for the case study to account for the risk vs. cost tradeoff, as shown in Figure 5 for both the Make and the Buy scenarios. For the Make scenario, the solution with the minimum risk (i.e., 9%) corresponds to the solution with the highest cost (i.e., \$2.7/kg H<sub>2</sub>) that also corresponds to the minimum production rate (i.e., using 200 tonnes of biomass/day); on the other hand, the solution for the minimum cost (1.98 \$/Kg H<sub>2</sub>) corresponds to the highest number of potential fatalities (100%), because the highest production rate. Notice at the right-hand side of this curve for the Make scenario, there is a rapid decrement of the cost with respect to a slow increment in the corresponding risk, and then the cost decreases slowly with respect to the corresponding increment in the risk. For the Buy scenario, a similar behavior appears; the solution for the minimum risk (18% fatalities) corresponds to the highest cost (\$1.57/kg H<sub>2</sub>) due to the lowest production rate (200 tonnes of biomass/day), and the solution with

the minimum cost (\$1.45/kg H<sub>2</sub>) corresponds to the solution with the highest risk (100% fatalities) due to the highest production rate. For the Buy scenario Pareto curve, there is a moderate decrement in the cost with respect to the increment in the risk (i.e., an increment in the production) at the right-hand side of the curve, and after a percentage of 40 of fatalities the costs remains constant with respect to the increment in the risk. As a conclusion, initially, as the cost of hydrogen decreases, the expected fatalities increase. However, there is limit after which the expected fatalities level off, indicating that above a certain production or purchase rate, the decision should be made based on economics. Finally, in this case study, the Buy scenario is consistently cheaper than the Make scenario. This is likely to change, as progress is made in biorefining technologies and if carbon credits or taxes are mandated.

## Conclusions

This article has introduced a multiobjective optimization approach to the simultaneous consideration of safety and economic objectives of biorefineries, in which risks and costs associated with the supply chain of biorefining have been accounted for. A superstructure has been developed to incorporate various configurations of interest including the Make vs. Buy scenarios. Potential fatalities have been correlated to production rates and impact distances through Probit functions. The Pareto curves provide the decision makers with a systematic tool for trading off the economic and risk objectives. The results for the case study have shown that the economic and safety objectives may contradict each other over certain ranges but not necessarily over the whole production/purchase ranges; we found that there is a production of purchase rate over which the decision should be on economics.

## Notation

### Indices/Sets

$i$  = index for feedstocks  
 $I$  = set of available feedstocks  
 $j$  = index for industrial facility  
 $J$  = set for facilities  
 $k$  = index for technologies  
 $K$  = set for technologies  
 $l$  = index for process sink (user)  
 $L$  = set for users

### Greek Symbols

$\alpha_{i,k}$  = conversion factor for the feedstock  $i$  using technology  $k$   
 $\delta_i^{\text{Cen\_max}}$  = maximum flow rate processed in the central facility  
 $\delta_i^{\text{max}}$  = maximum flow rate processed  
 $\delta_i^{\text{Cen\_min}}$  = minimum flow rate processed in the central facility  
 $\delta_i^{\text{min}}$  = minimum flow rate processed

### Parameters

$a_{i,j}$  = cost coefficient for the capital cost of the processing facility  $j$   
 $a_i^{\text{Cen}}$  = cost coefficient for the capital cost of the central processing facility  
 $b_{i,j}$  = cost coefficient for the capital cost of the processing facility  $j$   
 $b_i^{\text{Cen}}$  = cost coefficient for the capital cost of the central processing facility  
 $\text{Cost}_i^{\text{Biomass}}$  = unit feedstock cost

$\text{Cost}_i^{\text{Cen\_processing}}$  = unit processing cost for the feedstock  $i$  in the central facility  
 $\text{Cost}_k^{\text{Processing}}$  = unit processing cost for technology  $k$   
 $\text{Cost}_i^{\text{Processing}}$  = unit processing cost for feedstock  $i$   
 $\text{Cost}_{i,j}^{\text{Transp}}$  = unit transportation cost  
 $\text{Cost}_{i,j}^{\text{Transp\_Cen}}$  = unit transportation cost for central facilities  
 $\text{Cost}_{i,j}^{\text{Trans\_biofuels}}$  = unit transportation costs for biofuels  
 $\text{Fatalities}_i^{\text{Biomass}}$  = unit fatalities associated to produce  $i$   
 $\text{Fatalities}_i^{\text{Cen\_processing}}$  = unit fatalities associated to the processing in the central processing plant  
 $\text{Fatalities}_j^{\text{Processing}}$  = unit fatalities associated to the processing in the plant  $j$   
 $\text{Fatalities}_{i,j}^{\text{Transp}}$  = unit fatalities associated to transport  $i$  to the processing facility  $j$   
 $\text{Fatalities}_j^{\text{Trans\_biofuels}}$  = unit fatalities associated to the transportation of biofuels to facility  $j$   
 $\text{Fatalities}_i^{\text{Transp\_Cen}}$  = unit fatalities associated to transport  $i$  to the central processing facility  
 $H_Y$  = hours that the plant operates per year

### Variables

$\text{Cost}_i^{\text{Cen\_cap}}$  = capital cost for the central processing facility  
 $\text{Cost}_k^{\text{Capital}}$  = capital cost for the technology  $k$   
 $F_i$  = flow rate for the feedstock  $i$   
 $fc_i$  = flow rate for the feedstock  $i$  sent to the central processing facility  
 $f_{i,j}$  = flow rate for the feedstock  $i$  sent to the processing facility  $j$   
 $g^{\text{Cen}}$  = flow rate for the central facility  
 $H_j$  = flow rate produced in the facility  $j$   
 $h_{j,l}$  = flow rate of products sent from the facility  $j$  to  $l$   
 $M_j$  = product used in the plant  $j$  from the central plant  
 $m_{j,l}$  = flow rate sent from the central plant to the facility  $j$   
 $\text{Risk}$  = overall risk  
 $\text{TAC}$  = total annual cost  
 $\text{TCost}_i^{\text{Cen\_processing}}$  = total processing cost for the central facility  
 $\text{TCost}_j^{\text{Processing}}$  = total processing cost for the facility  $j$   
 $W_{i,j}$  = flow rate of product used in the plant  $j$   
 $Y_i^{\text{Cen}}$  = Boolean variable for the existence of the central processing facility  
 $y_i^{\text{Cen}}$  = binary variable for the existence of the central processing facility

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