

Environmental Impact Assessment of Chemical Process Using the Green Degree Method

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Achieving sustainable development while limiting environmental pollution is one of the main enormous challenges for chemical engineering at present. To develop and design a greener alternative to replace or retrofit a current polluted process, it is essential to establish a method for quantitatively evaluating the environmental impact of a chemical process so that its environmental performance can be improved by identifying and discovering the bottlenecks that cause the pollution. In this work, a green degree (GD) method is proposed to quantitatively evaluate the environmental impact of a chemical process and related energy-generation system. Definitions and calculation formulas of green degrees for a substance, a mixture, a stream, and a unit (process) are illustrated. The green degree is an integrated index that includes nine environmental impact categories (including global, air, water, and toxicological effects). Therefore, it is comprehensive for assessing and understanding the environmental performance of a complex multicomponent chemical system. Three illustrative case studies are presented to further describe and verify the applicability of the method: (1) solvent screening by comparing the green degree values of solvents, (2) process route screening for producing methyl methacrylate (MMA), and (3) green degree analysis of the methyl methacrylate process (*i*-C4 route) by integration with process simulation technology.

1. Introduction

The chemical industry is an important key to a nation's economic health; however, it is also one of the main sources of pollution.¹ Over the past several decades, significant efforts have addressed the reduction of industrial pollution, and the focus has gradually shifted from downstream pollution control to more aggressive practices of trying to prevent pollution.^{2,3} Today, cleaner production and green chemistry play a significant role in environmentally benign chemical process synthesis and design.⁴ One of the critical tasks for designing a green process is quantitative estimation of the environmental impacts on a substance, a stream, or a process. However, the material stream in a chemical process is a multicomponent mixture, and its integrative environmental impact should be estimated with respect to the environmental impact of each substance in the stream and the overall stream composition. Furthermore, the environmental impact of each substance is also regarded as an integrated value considering different categories of environmental impacts. In this work, a "green degree" method is proposed that, combined with process modeling technology, can be used to quantitatively identify and discover the bottlenecks of environmental impacts in a chemical process in order to improve its overall environmental performance.

Since the early 1990s, many works have been focused on environmentally benign process integration and design, such as the hierarchy approach to pollution prevention research,⁵ pollution prevention considering process waste and utility waste,^{6–8} the concept mass pinch tool to derive cost optimal mass-exchange networks (MENs) with minimum emissions,^{9–12} and design targets for minimum wastewater generation in process plants based on MENs.¹³ Recently, El-Halwagi et al. proposed a graphical technique called the property surplus diagram and cascade analysis technique to establish a targeting property-

based material reuse network.¹⁴ However, in each of these works, detailed environmental impact assessments were not studied systematically, and solely minimization of pollutants was taken into account.¹⁵

Quantitative evaluation of the environmental impacts of a chemical process has engaged wide attention. Sharratt et al. performed a systematic review of various environmental assessment methods and criteria for evaluating chemical processes.¹⁶ Pistkopoulos et al. proposed a methodology to estimate various environmental impacts using the cost function concept.¹⁷ The environmental hazard index (EHI) method was proposed and applied to chemical process selection in the early design stage to avoid processes with high potential pollution.¹⁸ The atmosphere hazard index (AHI), based on five environmental impact categories, was used to assess the inherent environmental friendliness of chemical processes to rank alternative routes.^{19–21} However, these environmental models, such as EHI and AHI, are so complicated and protracted that their applicability to chemical process design is limited. A short-cut method for environmental assessment with three levels of classification was proposed for early process development. In this method, a compound is evaluated using a simple ABC classification, i.e., high, medium, and low relevance for a given environmental impact category. For example, in the category of acute toxicity, a highly toxic substance is assigned to class A, a less toxic substance to class B, and a nontoxic substance to class C. Although this approach resolves the uncertainty of environmental impact,²² it does not allow for the quantitative estimation of environmental impacts.

Compared to the aforementioned methods,^{18–21} the waste reduction (WAR) algorithm has better practicability for chemical process design. It describes the flow of materials and generation of potential environmental impacts through a chemical process. Nine potential environmental impact indices are calculated from the process material balance, and a relative potential impact score for each chemical present is determined; this algorithm has also been extended to include energy generation and

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Table 1. Maximum Value of Each Environmental Impact Category φ_j^{\max} ($j = 1, 2, 3, \dots, 9$)

| | impact category j | φ_j^{\max} | units | reference substance | data source ^a |
|---|---|--------------------|---|------------------------------------|--------------------------|
| 1 | global warming potential (GWP) | 22200 | kg of CO ₂ /kg | sulfur hexafluoride | IPCC |
| 2 | ozone depleting potential (ODP) | 8.6 | kg of CFC-11/kg | 1,2-dibromotetrafluoroethane | WMO |
| 3 | photochemical ozone creation potential (PCOP) | 1.381 | kg of C ₂ H ₄ /kg | 1,3,5-trimethyl benzene | IMPACT 2002+ V2.01 |
| 4 | acidification potential (AP) | 1.88 | kg of SO ₂ equiv/kg | hydrogen sulfide | EDIP |
| 5 | eutrophication potential (EP) | 3.06 | kg of PO ₄ equiv/kg | phosphorus | IMPACT 2002+ V2.01 |
| 6 | ecotoxicity potential to water (EPW) | 233309.4 | 2,4-DB equiv/kg | cypermethrin | TRACI 2.0 method |
| 7 | ecotoxicity potential to air (EPA) | 96014.1 | 2,4-DB equiv/kg | tributyltin oxide | TRACI 2.0 method |
| 8 | human carcinogenic toxicity potential to water (HCPW) | 276989.96 | kg of C ₂ H ₃ Cl equiv/kg | phenesterin | IMPACT 2002+ V2.01 |
| 9 | human noncarcinogenic toxicity potential to water (HNCWP) | 317650 | kg of C ₂ H ₃ Cl equiv/kg | polychlorinated biphenyl, PCB-1254 | IMPACT 2002+ V2.01 |

^a IPCC = Intergovernmental Panel on Climate Change; WMO = World Meteorological Organization; EDIP = Environmental Design of Industrial Products, in Danish UMIP; TRACI 2.0 method, <http://www.epa.gov/ORD/NRMRL/std/sab/traci/>; IMPACT 2002 V2.01, from SimaPro 7.0 database.

economic considerations.^{23–26} Shannard et al. proposed the EFRAT (environmental fate and risk assessment) method and integrated it with HYSYS simulation software to establish a systematic framework for environmentally conscious chemical process design.^{27–29} The common feature of the methods listed above is that they are model-based, and both process models and environmental index models are included. Although the uncertainty of the impact index should be reduced further,¹⁵ linking environmental models to process models has been identified as one of the important needs of today's process design and simulation technology.³⁰

A comprehensive review of the research on environmental impact assessment associated with chemical process integration, design, and retrofitting is a considerable challenge. Even though quite a few works on environmental impact assessment methods have been published, there is still a variety of room for improvement, and the topic remains a hotspot for both environmental and chemical engineers. The existing methods are either too simple to express the holistic environmental impacts of a chemical process (such as a single index) or too complicated for a chemical engineer to apply because of the large quantity of environmental knowledge (such as AHI) required. Therefore, a practical environmental impact evaluation method mainly suited to chemical process design is urgently needed.

In this article, a green degree (GD) method is proposed for quantitatively assessing the environmental impacts of substances, streams, and units (processes) with the aid of the process simulation technology. Environmental issues, such as global warming, stratospheric ozone depletion, ecosystem health, atmospheric and aquatic acidification, smog formation, and so on, are converted to quantitative criteria, and then the criteria are integrated into the process simulation models, hence allowing the green degree values of substances, streams, and units (processes) to be calculated. Life cycle assessment (LCA) is a developing scientific methodology for assessing the environmental impacts of products and processes over the entire product life cycle;³¹ hence, the approach of LCA is applied herein for evaluating the green degree of a process. The present method is of significant value for pollution prevention and clean process design, and it is also easy to be applied and adopted by chemical engineers. Three cases are discussed to demonstrate the intended use of the method and verify its applicability and feasibility in chemical process assessment and design.

2. Green Degrees

2.1. Green Degree of a Substance. In chemical processes, the physical and chemical properties of a substance are important

when the substance is selected for use as a reactant, solvent, catalyst, refrigerant, and so on; indeed, such uses have brought great economic profits, but it is well-known that they can also cause serious environmental pollution. Thus, understanding the environmental performance of a substance and its potential environmental risk is as same important as understanding its other properties. In this work, a composite index, called the green degree, is proposed to quantitatively evaluate the comprehensive environmental impact of a substance based on nine environmental impact categories (listed in Table 1). The reason for selecting these nine environmental impacts is that they cover the potential environmental risks of a substance in terms of global, air, water, and toxicity impacts. The formula for calculating the green degree of a substance is as follows

$$GD_i^{\text{su}} = - \sum_{j=1}^9 (100\alpha_{ij}\varphi_{ij}^{\text{N}}) \quad (1)$$

$$\varphi_{ij}^{\text{N}} = \frac{\varphi_{ij}}{\varphi_j^{\max}}, \quad \varphi_j^{\max} = \max(\varphi_{ij})$$

$$\sum_{j=1}^9 \alpha_{ij} = 1$$

$$i = 1, 2, 3, \dots; j = 1, 2, 3, \dots, 9$$

Here, GD_i^{su} is the green degree of substance i . φ_{ij} is the environmental impact potential of substance i for impact category j , including the following nine categories: global warming potential (GWP), ozone depleting potential (ODP), photochemical ozone creation potential (PCOP), acidification potential (AP), eutrophication potential (EP), ecotoxicity potential to water (EPW), ecotoxicity potential to air (EPA), human carcinogenic toxicity potential to water (HCPW), and human noncarcinogenic toxicity potential to water (HNCWP). φ_{ij}^{N} is the relative impact potential obtained by normalizing φ_{ij} by φ_j^{\max} , which is the maximum value for category j among all of the substances reported. The reason for determining φ_j^{\max} as the normalization benchmark is that, for substance i , the value of φ_{ij}^{N} for each category is normally from 0 to 1, which gives a value of environmental impact relative to the worst one, i.e., φ_j^{\max} . In particular, even if a newly discovered or synthesized substance had a φ_{ij} value that was larger than φ_j^{\max} , so that its φ_{ij}^{N} value was correspondingly larger than 1, this situation would not influence the relative value of a green degree. In general, such an event is likely to happen only rarely during a relatively long period. Other published research has chosen

national emissions data for normalization,³² which might cause some uncertainty because of the different standards in different regions and countries. $\alpha_{i,j}$ is the weighting factor of substance i for impact category j . Other published works^{24–26,33} have indicated that the weighting factor for each category was difficult to determine because it was influenced by a number of factors, such as regulations, local limitations, personal preferences, or the requirements of a project. However, for a given problem, we can use the same set of weighting factor values to ensure that the results are comparable.

According to eq 1, GD_i^{su} generally ranges between -100 and 0 , where -100 represents a substance that has the worst environmental performance and 0 represents a substance whose presence does not produce any additional pollution impact on the environment, such as oxygen, pure water, etc.

Definition of the units of GD_i^{su} is always a matter of debate. Published works have not reached a common approach to this problem either. For example, Young et al. used potential environmental impact (PEI) as a unit to represent the environmental impacts, such as PEI/h.²⁴ Chen and Shonnard did not provide a clear description of the units of their environmental index.²⁹ Gunasekera and Edwards considered the CAH (chemical atmospheric hazards) index to be a dimensionless quantity.¹⁹ For convenience in assessing processes, we defined the units of GD_i^{su} for substance i as green degrees per kilogram of substance (gd/kg of substance). The reason for taking the benchmark unit in terms of kilograms is that all of the impact potentials $\varphi_{i,j}$ are based on mass (see Table 1). The maximum value of each environmental impact potential φ_j^{max} reported in Table 1 is based on the current published data on the nine environmental impact categories.

2.2. Green Degrees of a Mixture, GD^{mix} , and a Stream, GD^S . Equation 1 gives the method for calculating the green degree of a substance, but for a chemical process, almost all operations involve multicomponent mixtures or streams. We therefore define the green degree of a mixture, GD^{mix} , as

$$GD^{mix} = \sum_{k=1}^m GD_k^{su} x_k, \quad k = 1, 2, 3, \dots, m \quad (2)$$

GD^{mix} has units of green degrees per kilogram of mixture (gd/kg of mixture). GD_k^{su} is the green degree of component k , and x_k is the mass fraction of component k in the mixture. Equation 2 can also be used to calculate the green degree of a tank filled with chemicals in a chemical plant.

The green degree of a material stream in a chemical process, GD^S , can be calculated by

$$GD^S = F \times \sum_{k=1}^m GD_k^{su} x_k, \quad k = 1, 2, 3, \dots, m \quad (3)$$

where the units of GD^S are green degrees per hour (gd/h). F is the mass flow rate of the stream (kg/h), GD_k^{su} is the green degree of component k , and x_k is the mass fraction of component k in the stream.

2.3. Green Degree Production of a Unit (or a Process), ΔGD^u . A typical process setup consists of many pieces of equipment (units), such as reactors, separators, columns, mixers, and so on. Physical and chemical conversions occur in these units under a variety of operating conditions, and products, byproducts, and waste are produced by the process. For a nonstandard operating state, such as an explosion, the environmental impact of such a situation is caused by all of the reactants

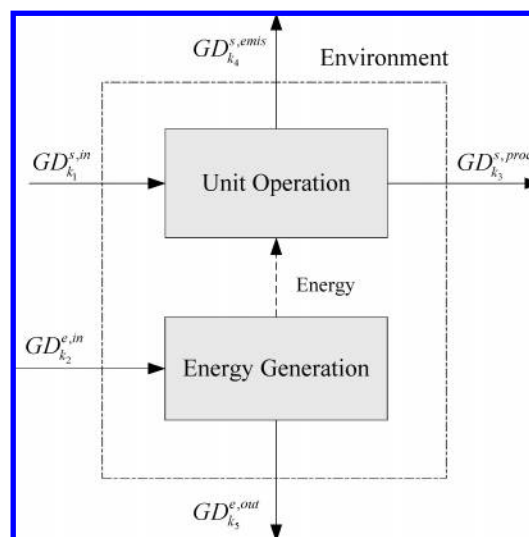


Figure 1. Input–output relationship of the unit operation associated with the energy-generation system.

released to the environment. However, for a normal operating situation, the streams of reactants, solvents, catalysts, etc., with different green degree values are charged in to a unit, and fluent flows out of the unit, which causes a change in green degrees for the unit. In this work, we propose the concept of green degree production of a unit to express the change that is caused by the material and energy conversions taking place in the unit; that is, the green degree production of a unit is the additional environmental impact caused by the unit operation. Green degree production is particularly useful for assessing the environmental performance of a unit, and with the assessment results, a measure for improving environmental performance can be proposed.

Figure 1 shows the input and output relationship of a unit in a steady operation process associated with an energy-generation system. It was found that both the local on-site emissions and emissions generated by centralized power generation corresponding to the amount of power imported (or exported) need to be included to obtain a true picture of the waste emissions in a process.³⁴ In Figure 1, a unit operation represents the system in which the physical and chemical conversions of the raw materials occur, and energy generation provides the required energy (power and heat) to the unit operation. Considering the boundary shown in Figure 1, the green degree production of a unit, ΔGD^u (gd/h), is assigned to represent the additional environmental impact of this unit operation that is associated with energy consumption. ΔGD^u is formulated as

$$\Delta GD^u = \sum_{k_3} GD_{k_3}^{s,proc} + \sum_{k_4} GD_{k_4}^{s,emis} + \sum_{k_5} GD_{k_5}^{e,out} - \sum_{k_1} GD_{k_1}^{s,in} - \sum_{k_2} GD_{k_2}^{e,in} \quad (4)$$

In eq 4, $GD_{k_1}^{s,in}$ is the input green degree value of a stream into the unit operation, and k_1 indicates the input stream, such as a raw material, solvent, or catalyst. $GD_{k_2}^{e,in}$ is the green degree value of an energy source fed into the energy-generation system, where k_2 refers to the energy source, such as natural gas, coal, or oil. $GD_{k_3}^{s,proc}$ is the green degree value of the process stream from one unit to the others, and $GD_{k_4}^{s,emis}$ is the green degree value of the emission or discharge stream from the unit directly into the environment. $GD_{k_5}^{e,out}$ is the green degree value of an emission or discharge stream from the energy-generation system into the environment.

Table 2. 1995 Emissions from Fossil-Fuel Electricity Plants by Fuel Type³⁵

| fuel | net generation (10 ⁶ kWh) | emissions (10 ³ short tons) | | |
|-----------|---|--|-----------------|-----------------|
| | | SO ₂ | NO _x | CO ₂ |
| coal | 1652914 | 11248 | 6508 | 1752527 |
| gas | 307306 | 1 | 533 | 161969 |
| petroleum | 60844 | 321 | 92 | 50878 |

Table 3. Waste Emissions and Green Degree Values of Electric Plants with Different Fuels

| fuel | waste emissions (kg/M kcal) | | | GD ^e (gd/M kcal of energy) |
|---|-----------------------------|-----------------|-----------------|--|
| | SO ₂ | NO _x | CO ₂ | |
| coal | 7.913 | 4.578 | 1232.9 | -380.4 |
| gas | 0.00378 | 2.017 | 612.87 | -163.11 |
| petroleum | 6.135 | 1.758 | 972.3 | -290.39 |
| green degree value (gd/kg of emission) | -6.296 | -4.834 | -0.2502 | |

A value of $\Delta\text{GD}^u > 0$ indicates that the unit operation is benign to the environment, for example, a process that fixes CO₂ while generating an organic compound and oxygen as happens in leaves in nature. Correspondingly, $\Delta\text{GD}^u < 0$ indicates that the unit operation adds pollution to the environment, a simple example of which is a coal-fired furnace, which produces energy but also releases a great deal of waste gas to the atmosphere. If a unit does not generate extra impacts on the environment, then $\Delta\text{GD}^u = 0$. Equation 4 provides a feasible and convenient judgment criterion for assessing the environmental impacts of a unit. The larger the ΔGD^u value, the better the holistic environmental performance of a unit. Equation 4 is also suitable for chemical processes.

$\text{GD}_{k_5}^{\text{e,out}}$ in eq 4 indicates the green degree value associated with the energy-generation system for a process. For the same energy demand, different energy sources (such as coal, oil, natural gas, etc.) produce different amounts of waste and cause different environmental impacts. In this work, our emphasis is focused on unit operations (see Figure 1), so we exclude any environmental impacts arising from the mining and transportation of energy sources. Thus, $\text{GD}_{k_5}^{\text{e,out}}$ equals the green degree value of the wastes emitted from the process for generating the power. k_5 is the emission stream from the energy-generation system, including components such as CO₂, SO_x, and NO_x. $\text{GD}_{k_5}^{\text{e,out}}$ can be calculated with eq 3.

The amount of pollutants emitted by combusting the energy resource is dependent on the fuel type and the applied technology. Using the waste emission data from the fired power plant

systems reported in Table 2,³⁵ the green degree values of power generation systems with different fuel types can be estimated as shown in Table 3.

Thus, using eqs 1–4 and Table 3, combined with process simulation technology, the green degree values of substances, mixtures, streams, units, and processes, as well as energy-generation systems, can be estimated quantitatively.

3. Applications and Case Studies

3.1. Solvent Screening. In the chemical industry, use of solvents is common in many processes, e.g., catalytic reactions, extractive separations, absorptions, stripping operations, crystallizations, and so on. Use of a solvent can facilitate process operations, increase reaction conversion and selectivity, improve product purities and yields, and reduce energy consumption. For instance, when extractive distillation is used in place of pressure-swing distillation, the energy requirements are greatly reduced. However, although use of solvents might offer obvious advantages, environmental pollution caused by solvent release limits their utilization. This is mainly because most solvents are volatile and generate low levels of ozone during smog formation reactions in the atmosphere, as well as causing health concerns for workers and the general population in the vicinity of the facilities. According to Toxic Release Inventory (TRI) data, 5 of the top 10 chemicals released or disposed are solvents, such as methanol, toluene, etc. The total quantity of these chemicals released or disposed accounts for 27% of the total quantity of TRI chemicals released and disposed.³⁶ Therefore, understanding the potential environmental impacts of solvents is critical for screening possible solvents during chemical process design.

As a case study, we calculated the green degree values of some commonly used solvents with eq 1 to make a quantitative comparison that can provide guidance for a process designer in selecting solvents. The results are reported in Table 4 and Figure 2.

Figure 2 shows the green degree values of selected solvents. Phenixin has the lowest green degree value, because its GWP, ODP, EPW, HCPW, and HNCPW values are highest among the selected solvents, which means that phenixin had better not be considered as a solvent during process design. Chloroform also has a low green degree value because of its high GWP and EPW values. Hydrocarbon series solvents, such as propane, butane, pentane, and hexane, have relatively high green degree

Table 4. Environmental Impact Potential Values, φ_{ij} , of Categories j and Green Degree Values, GD_i^{su} , of Solvents i

| i | j | | | | | | | | | GD_i^{su} |
|------------------|------|------|--------|----|----|---------|-----------------------|---------|------------------------|---------------------------|
| | GWP | ODP | PCOP | AP | EP | EPW | EPA | HCPW | HNCPW | |
| propane | — | — | 0.176 | — | — | — | — | — | — | -1.4163 |
| butane | — | — | 0.352 | — | — | — | — | — | — | -2.8321 |
| pentane | — | — | 0.395 | — | — | — | — | — | — | -3.1781 |
| hexane | — | — | 0.482 | — | — | 0.8004 | 1.3×10^{-6} | 0 | 1.006×10^{-3} | -3.9198 |
| cyclohexane | — | — | 0.29 | — | — | — | — | — | — | -2.3332 |
| octane | — | — | 0.453 | — | — | — | — | — | — | -3.6447 |
| benzene | — | — | 0.218 | — | — | 1.629 | 6.34×10^{-3} | 0.1181 | 1.3567 | -7.3156 |
| toluene | — | — | 0.637 | — | — | 1.6269 | 2.5×10^{-3} | — | — | -5.4919 |
| <i>o</i> -xylene | — | — | 1.053 | — | — | 5.762 | 1.76×10^{-3} | — | — | -8.9502 |
| <i>m</i> -xylene | — | — | 1.108 | — | — | 7.676 | 9.99×10^{-4} | — | — | -9.3958 |
| chloromethane | 16 | 0.02 | 0.005 | — | — | 0.4085 | 0.005 | — | — | -0.6721 |
| dichloromethane | 10 | — | 0.068 | — | — | 0.4394 | 0.01386 | 0.1999 | 0.2612 | -3.0986 |
| chloroform | 30 | — | — | — | — | 1.8123 | 0.0398 | 1.4754 | 0.1500 | -12.669 |
| phenixin | 1800 | 1.2 | — | — | — | 2.875 | 0.0178 | 24.6941 | 7.7878 | -32.8797 |
| methanol | — | — | 0.14 | — | — | 0.0106 | 0.0192 | — | 0.000823 | -3.3517 |
| phenol | — | — | — | — | — | 0.3529 | 0.05439 | — | 0.000768 | -6.3137 |
| acetone | — | — | 0.094 | — | — | 0.00962 | 0.0132 | — | 0.006538 | -2.3072 |
| 2-butanone | — | — | 0.0373 | — | — | 0.01827 | 0.00957 | — | 0.000377 | -1.4098 |

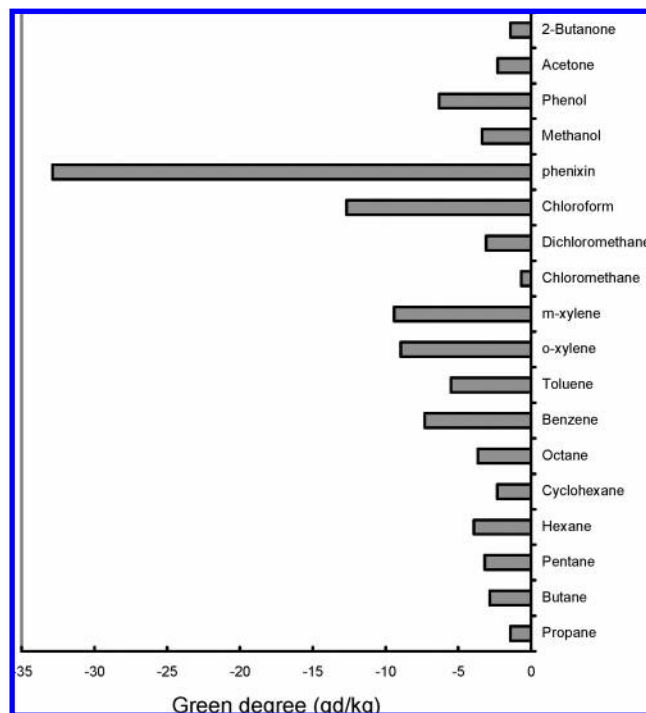


Figure 2. Green degree values of selected commonly used solvents.

values, but with increasing number of carbons, the green degree value of the hydrocarbon decreases.

The above analysis shows that the green degree method provides a feasible approach for quantitatively assessing the environmental impact of a solvent. Compared with the traditional method, which takes environmental potential values, ϕ_{ij} , from one or several impact categories j (such as GWP, AP, etc.) to be criteria for evaluating the environmental performance of a solvent, the present method can help avoid or weaken the possible subjectivity involved in using the traditional method. For example, when two solvents are compared, it is highly likely that not all of the categories will have smaller or larger impact potential values for one solvent compared to another, which would make judging which solvent is greener difficult. On the other hand, a lack of environmental data often makes comparisons using a single index method unfeasible. In contrast, use of the composite green degree index, which integrates nine potential values, can avoid this unfeasibility. Generally, the green degree method can serve as a bridge to link the chemical engineer and the environmental engineer, helping them to understand environmental performance when they design a new process or retrofit an old one.

3.2. Route Selection for a Chemical Process. To further verify the proposed method, we consider a typical chemical process, i.e., methyl methacrylate (MMA) production, as a study case. In industrial practice, at least six routes to produce MMA, based on different raw materials and technologies, are used. The six routes are as follows:²⁰ (1) *tert*-butyl alcohol (TBA), (2) isobutylene (*i*-C4), (3) propylene (C3), (4) ethylene via methyl propionate (C2/MP), (5) ethylene via propionaldehyde (C2/PA), and (6) acetone cyanohydrin (ACH).

For these six routes, the feedstocks and estimated inventories are listed in Table 5.^{18,19} We calculated the green degree value of each route by considering its chemical inventories. With eq 1, we determined the green degree value for each substance (gd/kg), as well as its total green degree contribution according to the estimated inventories (see Table 5). For the substances

Table 5. Green Degree Values of Six Routes for Producing MMA

| route | substance | estimated inventory (kg) | gd/kg | gd | total (route) |
|--------------|----------------------------|--------------------------|---------|----------------------|-----------------------|
| TBA | methacrolein | 41 | 0 | 0 | -9.3012×10^3 |
| | methacrylic acid | 35 | -0.219 | -7.654 | |
| | methanol | 2024 | -3.352 | -6.784×10^3 | |
| | methyl methacrylate | 6309 | -0.271 | -1.713×10^3 | |
| | oxygen | 7 | 0 | 0 | |
| | <i>tert</i> -butyl alcohol | 4673 | -0.171 | -797.068 | |
| | water | 10 | 0 | 0 | |
| | | | | | |
| | | | | | |
| | | | | | |
| <i>i</i> -C4 | isobutylene | 3540 | -1.009 | -3.572×10^3 | -1.2076×10^4 |
| | methacrolein | 37 | 0 | 0 | |
| | methacrylic acid | 27 | -0.219 | -5.904 | |
| | methanol | 2025 | -3.352 | -6.787×10^3 | |
| | methyl methacrylate | 6305 | -0.271 | -1.713×10^3 | |
| | oxygen | 25 | 0 | 0 | |
| | water | 19 | 0 | 0 | |
| | | | | | |
| | | | | | |
| | | | | | |
| C3 | carbon monoxide | 5.6 | -0.436 | -2.444 | -4.3468×10^4 |
| | hydrogen fluoride | 9 | -0.946 | -8.511 | |
| | isobutyric acid | 52 | -0.213 | -11.064 | |
| | methacrylic acid | 29 | -0.219 | -6.3412 | |
| | methanol | 2022 | -3.352 | -6.777×10^3 | |
| | methyl methacrylate | 6309 | -0.271 | -1.713×10^3 | |
| | oxygen | 4.3 | 0 | 0 | |
| | propylene | 5394 | -6.479 | -3.495×10^4 | |
| | water | 3 | 0 | 0 | |
| | | | | | |
| C2/MP | carbon monoxide | 5.9 | -0.4363 | -2.574 | -1.8097×10^4 |
| | ethylene | 1774 | -1.609 | -2.855×10^3 | |
| | methanol | 4034 | -3.352 | -1.352×10^4 | |
| | methyl propionate | 20 | 0 | 0 | |
| | methylal | 34 | -0.264 | -8.973 | |
| | methyl methacrylate | 6300 | -0.271 | -1.713×10^3 | |
| | water | 1.7 | 0 | 0 | |
| | | | | | |
| | | | | | |
| | | | | | |
| C2/PA | carbon monoxide | 5.8 | -0.436 | -2.531 | -3.3457×10^4 |
| | ethylene | 1774 | -1.609 | -2.855×10^3 | |
| | formaldehyde | 1890 | -11.704 | -2.212×10^5 | |
| | hydrogen | 127 | 0 | 0 | |
| | methacrolein | 46 | 0 | 0 | |
| | methacrylic acid | 19 | -0.219 | -4.155 | |
| | methanol | 2016 | -3.352 | -6.757×10^3 | |
| | methyl methacrylate | 6323 | -0.271 | -1.713×10^3 | |
| | oxygen | 5.7 | 0 | 0 | |
| | propionaldehyde | 1.1 | -1.284 | -1.412 | |
| ACH | water | 9.6 | 0 | 0 | -3.5597×10^4 |
| | acetone | 3657 | -2.307 | -8.435×10^3 | |
| | acetone cyanohydrin | 33 | 0 | 0 | |
| | ammonia | 1075 | -10.799 | -1.161×10^4 | |
| | ammonium bisulphate | 5.4 | 0 | 0 | |
| | carbon dioxide | 5.5 | -0.250 | -1.376 | |
| | hydrogen cyanide | 2.3 | -16.04 | -36.914 | |
| | methacrylamide | 0.66 | 0 | 0 | |
| | methane | 1215 | -5.765 | -7.005×10^3 | |
| | methanol | 2014 | -3.352 | -6.75×10^3 | |
| | methyl methacrylate | 6328 | -0.271 | -1.718×10^3 | -3.5597×10^4 |
| | nitrogen | 3.5 | 0 | 0 | |
| | oxygen | 23 | 0 | 0 | |
| | sulfur dioxide | 42 | -0.591 | -24.823 | |
| | sulfuric acid | 9.4 | -0.384 | -3.611 | |
| | sulfur trioxide | 22.4 | -0.473 | -10.591 | |
| | water | 22 | 0 | 0 | |
| | | | | | |
| | | | | | |
| | | | | | |

listed in Table 5, we found that the virulent hydrogen cyanide has the lowest green degree value; the green degree value of formaldehyde is also low because its high POCP, AP, and EPW. The reason for ammonia's low green degree value is that it has

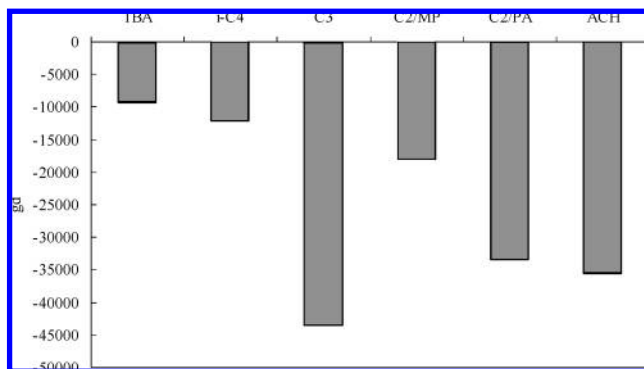


Figure 3. Green degree values of six routes for producing MMA.

a high AP, the same as that of hydrogen sulfide. Propylene also has a low green degree value because of the contribution of its high PCOP of 1.123 kg of C₂H₄/kg (the PCOP value of the reference substance is 1.381 kg of C₂H₄/kg in Table 1). The low green degree value of methane is caused by its well-known high GWP.

The estimated green degree value for each route is reported in Table 5 and Figure 3. The results indicated that the green degree order of the six considered routes is TBA > *i*-C4 > C2/MP > C2/PA > ACH > C3. The TBA and *i*-C4 routes use similar technologies but with different feedstocks, i.e., *tert*-butyl alcohol for the TBA route and isobutylene for the *i*-C4 route (see Table 5). Both are accepted as clean technologies. However, the green degree value of isobutylene is lower than that of *tert*-butyl alcohol because the former has a higher PCOP value (0.627 kg of C₂H₄/kg) than the latter (0.106 kg of C₂H₄/kg), which makes the green degree value of TBA larger than that of *i*-C4. Compared with C2/MP route, the C2/PA route has a lower green degree value because of the contribution of using formaldehyde. The ACH route is often considered a contaminated process in industry; however, this study shows that the C3 route is slightly higher in terms of potential hazards than the ACH route. Although the ACH route uses virulent hydrogen cyanide as a material, only a small quantity of hydrogen cyanide is used, and in fact, the largest contributions to the environmental impact of this route are from ammonia (−10.799 g/d/kg), methane (−5.765 g/d/kg), and methanol (−3.352 g/d/kg). In contrast, the C3 route uses a large quantity of propylene (−6.479 g/d/kg), which gives it a lower green degree value than the other routes.

The above analysis indicates that the proposed method offers a general environmental impact assessment method for chemical routes and is extremely valuable for screening and comparing different approaches in the early design stage of a process. Such a quantitative environmental impact assessment provides an important tool for cleaner and greener process optimization and integration, as it translates rough qualitative descriptions (for example, using only general descriptions of virulent or low-poison feedstocks) into a much more quantitative assessment and evaluation. Therefore, it should provide a comprehensive measurement tool for improving the environmental performance of a chemical process, allowing highly polluting feedstocks or solvents to be replaced with greener chemicals.

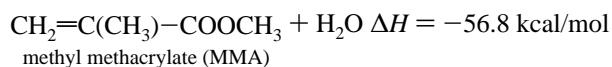
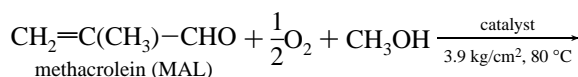
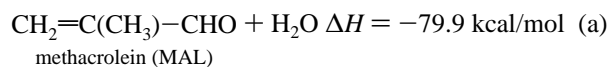
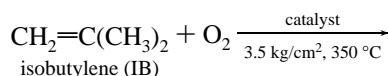
The ordering of the MMA routes obtained in this work does not agree well with the results from the literature, which have the order C2/MP > C3 > *i*-C4 > TBA > ACH > C2/PA according to the method of estimating predicted environmental concentrations (PEC method).²¹ The main reason for the difference is that the green degree (GD) method emphasizes

the relative environmental impacts of chemicals or processes, not the “true” impact that is calculated by the PEC method. The units of all nine impact categories are “kilograms of substance (equivalents)/kilogram of substance”, which makes it easy to estimate environmental impacts. Furthermore, the green degree method ignores the differences in the dispersion characteristics of chemicals, whereas it is difficult to establish the boundaries of a compartment where one impact category of a substance does react when the PEC method is used. Therefore, the GD method is much more convenient for use during process design.

3.3. Green Degree Assessment of a Chemical Process. In a chemical process, the green degree value of a given quantity of material flow and energy flow can generally be regarded as the impact that this material and energy would have on the environment if it were completely released into the environment, which means a kind of inherent and minimum environmentally benign degree, which can be estimated using eq 3. A relatively mature process simulation technology can provide valuable material and energy flow information comparable to that available from industry; therefore, combining simulation technology with the GD method can predict the green degree production of a unit and a process. We took the MMA manufacture process with the *i*-C4 route as a case study to show how to use GD method to analyze and evaluate the environmental performances of units and subsystems in a chemical process.

The *i*-C4 route was established commercially by companies in Japan where a new supply of hydrogen cyanide (HCN) could not be expected, and it is also regarded as a green technology because of the absence of HCN in the ACH method. Now, some Japanese companies are making an effort to develop new technologies, such as new catalysts to improve the conversion ratios and selectivities of reactions. Today in Japan, more than one-half of MMA production capacity comes from the *i*-C4 route. In addition to those in Japan, direct oxidation plants are operating in Korea, Singapore, and Thailand.³⁷

The principle flowsheet diagram of the MMA process with the *i*-C4 route is shown in Figure 4, which is derived from an SRI report.³⁷ The recycling streams are broken down to facilitate the assessment of the green degree values of different parts of the overall process. As shown in this flowsheet, two reaction steps are included: First, an oxidation reaction occurs to produce methacrolein from feedstocks of isobutylene (IB) and air/oxygen (see eq a). Second, methacrolein (MAL), methanol, and air are mixed, and MMA is produced by a direct oxidation–esterification reaction (see eq b). After extraction and distillation, high-purity MMA product is obtained. The main units in this process are an IB oxidation reactor (R101), a quench tower (C101), a dehydration tower (C102), a MAL absorber (C103), a MAL esterification reactor (R201), a methanol column (C201), and a MMA drying column (C202).



(b)

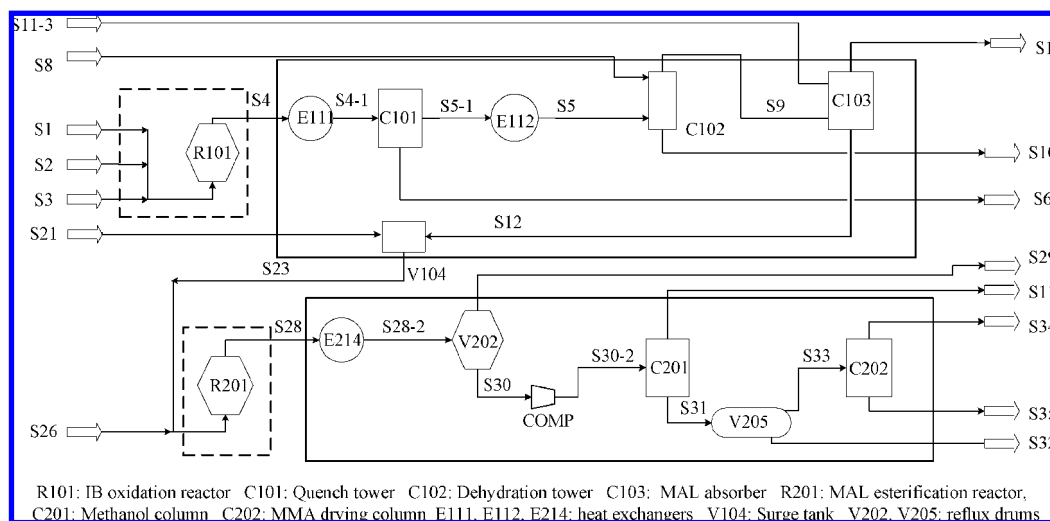


Figure 4. Principle process diagram of MMA production by the *i*-C4 route.

In Figure 4, a mixture of isobutylene, oxygen (or air), and steam is preheated to 350 °C and pumped into the MAL oxidation reactor (R101) at 3.5 atm to produce methacrolein (MAL); small quantities of acetone and butane are produced as byproducts. This is an exothermic reaction, and after passing through the heat exchanger, the MAL stream is cooled to 100 °C and then delivered into the quenching tower (C101), where about 70% of the water is removed. The MAL stream is further dehydrated in an absorber (C102), and unreacted methanol in the MAL stream is absorbed. The low-water-concentration MAL stream is delivered to the MAL absorber (C103), and MAL is absorbed with methanol solution to separate the waste gas (mainly nitrogen). The liquid effluent containing MAL and methanol is sent to the MMA esterification reactor (R201) to react with oxygen from an air stream for synthesis of the MMA product. The product stream from unit R201 is cooled in heat exchanger E214 to about 45 °C, and then the liquid MMA solution is separated from the vapor in a flash drum (V202). The liquid effluent from V202 is pumped into the methanol column (C201) to separate methanol, and about 98% of the methanol and other organic impurities is removed in C201. The MMA stream from C201 is delivered into a liquid–liquid reflux drum (V205) to separate MMA and water. The MMA effluent from V205 is dried in the MMA drying column (C202), and the MMA product (≥ 98.5 wt %) is obtained. The process was simulated with Aspen Plus to calculate the detailed material and energy flows.

The flowsheet division method was used to divide the overall process into several parts depending on the process features, such as reaction, separation, and so on, and then assess and compare the green degree values of the various parts. The advantage of this method is that the environmental impact “bottlenecks” can be identified, and then the possible effective measures can be considered to improve the environmental performance of each part and then the overall process. In this work, we divided the overall MMA process into four parts (indicated by regions enclosed in dashed and solid lines in Figure 4): Part 1 is the isobutylene oxidation reaction, including unit R101. Part 2 is MAL separation, including units E111, E112, C101, C102, C103, and V104. Part 3 is the MMA reaction, including unit R201. Finally, part 4 is MMA separation and purification, including units: E214, C201, C202, V201, and V201.

The specifications of the main stream are listed in Table 6. The simulation was based on the production of 110800 ton/

year of MMA product with a 0.9 on-stream factor. Table 6 lists the main input and output streams of the four parts in the MMA process, along with the green degree value of each stream. With eq 4, the green degree production, ΔGD^u , of each part was calculated. From the results, we can determine which part has the highest environmental impact and the corresponding improvement measures that could be taken.

Figure 5 shows that the green degree production order of the four parts is part 1 > part 3 > part 2 > part 4, which means that part 1 has the highest green degree production and part 4 has the lowest green degree production. In part 1, after the reaction, the feedstock isobutylene and methanol with lower green degree values are converted to MAL, causing an increase in the green degree value in this part. In part 3, the intermediate product MAL and more methanol are sent to the MMA esterification reactor (R201) to react with oxygen to produce the MMA product stream. Considering the input streams S23 and S26 and the output stream S28, because of a large amount of methanol in the input stream, which has a lower green degree value, is used up during the reaction, the methanol flow rate in the output stream decreases, and the total green degree production in part 3 increases. Even though the MMA product decreases the green degree production slightly, the aggregate result is that the green degree production in part 3 increases, which means that part 3 also is an environmentally benign process that does not produce any extra environmental impact. In part 4, the low green degree production is mainly caused by the energy consumption required for separating MMA and the unreacted materials and byproduct in C201, as well as recovering unreacted surplus methanol in C202, which means that the emissions from the energy-generation system make a great contribution to the reduction in green degree production.

Judging from the calculation results, we can determine which part is the most significant contributor to the overall environmental impacts in this MMA process. According to the results, efforts should be made in part 4 to increase its green degree value by using a low-energy-consumption separation technology.

Introduction of the green degree method into chemical process design will be a great improvement in design for environment (DfE) efforts because it can quantitatively evaluate the green degree values of streams, units and processes, in addition to the traditional mass and energy balances, which will be more significant for sustainable process design and development.

Table 6. Main Input and Output Streams of the Four Parts of the MMA Process^a

(a) Specifications of the Input and Output Streams in Part 1

| stream no. | input | | | output |
|--|----------|--------|---------|---------|
| | S1 | S2 | S3 | S4 |
| temperature (K) | 623.15 | 623.15 | 623.15 | 623.15 |
| pressure (atm) | 3.5 | 3.5 | 3.5 | 3.5 |
| flow rate (kg/h) | 10610 | 5978 | 76878 | 93465.9 |
| green degree (gd/h) | -10898.0 | 0 | -1670.8 | -2619.0 |
| stream composition (mass fraction) | | | | |
| O ₂ | 0 | 0 | 0.140 | 0.043 |
| H ₂ O | 0 | 1.000 | 0.012 | 0.115 |
| MAL | 0 | 0 | — | 0.122 |
| CH ₄ O | 0 | 0 | 0.003 | 0.002 |
| IB | 1.000 | 0 | 0.002 | 0.003 |
| MMA | 0 | 0 | 0 | 0 |
| C ₂ H ₄ O ₂ | 0 | 0 | 0 | 0 |
| C ₃ H ₆ O | 0 | 0 | 0 | 0 |
| CH ₂ O | 0 | 0 | 0 | 0 |
| MAA | 0 | 0 | 0 | 0.004 |
| C ₄ H ₁₀ | 0 | 0 | 0.001 | 0.002 |
| N ₂ | 0 | 0 | 0.822 | 0.676 |
| CO | 0 | 0 | 0.009 | 0.014 |
| CO ₂ | 0 | 0 | 0.011 | 0.018 |

(b) Specifications of the Input and Output Streams in Part 2

| stream no. | input | | | | output | | | |
|--|---------|-----------|----------|----------|--------|--------|----------|-----------|
| | S4 | S11-Re | S8 | S21 | S6 | S10 | S13 | S23 |
| temperature (K) | 623.15 | 293.15 | 318.15 | 333.15 | 373.15 | 327.11 | 300.28 | 313.46 |
| pressure (atm) | 3.5 | 2.5 | 2.5 | 1.0 | 3.0 | 2.4 | 1.5 | 3.9 |
| flow rate (kg/h) | 93465.9 | 50762.0 | 5745.6 | 7389.0 | 8129.9 | 4035.2 | 82554.52 | 63642.9 |
| green degree (gd/h) | -2619.0 | -141438.7 | -18409.1 | -23272.8 | -87.8 | -110.0 | -35482.7 | -150059.2 |
| stream composition (mass fraction) | | | | | | | | |
| O ₂ | 0.0428 | 0 | 0 | 0 | 0 | 0.0001 | 0.0483 | 0 |
| H ₂ O | 0.1148 | 0.0254 | 0.0291 | 0.0184 | 0.9275 | 0.6089 | 0.0011 | 0.0356 |
| MAL | 0.1225 | 0.0390 | 0.0062 | 0.0362 | 0.0211 | 0.3804 | 0.0045 | 0.1860 |
| CH ₄ O | 0.0024 | 0.8221 | 0.9552 | 0.9392 | 0.0028 | 0.0073 | 0.1202 | 0.7090 |
| IB | 0.0029 | 0 | 0 | 0 | 0 | 0.0008 | 0.0030 | 0.003 |
| MMA | 0 | 0.1135 | 0.0096 | 0.0061 | 0 | 0 | 0.00198 | 0.0675 |
| C ₂ H ₄ O ₂ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| C ₃ H ₆ O | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| CH ₂ O | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| MAA | 0.0042 | 0 | 0 | 0 | 0.0480 | 0 | 0 | 0 |
| C ₄ H ₁₀ | 0.0022 | 0 | 0 | 0 | 0.0005 | 0.0006 | 0.0023 | 0.0002 |
| N ₂ | 0.6761 | 0 | 0 | 0 | 0 | 0.0013 | 0.7646 | 0.0010 |
| CO | 0.0138 | 0 | 0 | 0 | 0 | 0 | 0.0156 | 0 |
| CO ₂ | 0.0183 | 0 | 0 | 0 | 0 | 0.0003 | 0.0205 | 0.0004 |

(c) Specifications of the Input and Output Streams in Part 3

| stream no. | input | | output |
|--|-----------|---------|-----------|
| | S23 | S26 | S28 |
| temperature (K) | 313.46 | 353.15 | 353.15 |
| pressure (atm) | 3.9 | 3.9 | 3.9 |
| flow rate (kg/h) | 62642.9 | 14052.3 | 76695.2 |
| green degree (gd/h) | -150059.2 | 0.0 | -141009.9 |
| stream composition (mass fraction) | | | |
| O ₂ | 0 | 0.2180 | 0.0026 |
| H ₂ O | 0.0356 | 0.0188 | 0.0343 |
| MAL | 0.1860 | 0 | 0.0258 |
| CH ₄ O | 0.7090 | 0 | 0.5265 |
| IB | 0.0003 | 0 | 0.0002 |
| MMA | 0.0675 | 0 | 0.2663 |
| C ₂ H ₄ O ₂ | 0 | 0 | 0 |
| C ₃ H ₆ O | 0 | 0 | 0 |
| CH ₂ O | 0 | 0 | 0 |
| MAA | 0 | 0 | 0 |
| C ₄ H ₁₀ | 0.0002 | 0 | 0.0002 |
| N ₂ | 0.0010 | 0.7633 | 0.1407 |
| CO | 0 | 0 | 0 |
| CO ₂ | 0.0004 | 0 | 0.0034 |

Table 6 (Continued)

| stream no. | input | | | output | | |
|--|-----------|-----------|---------|---------|---------|---------|
| | S28 | S11 | S29 | S32 | S34 | S35 |
| temperature (K) | 353.15 | 293.15 | 318.15 | 380.37 | 345.92 | 420.78 |
| pressure (atm) | 3.9 | 2.75 | 3.5 | 2.98 | 2.0 | 3.45 |
| flow rate (kg/h) | 76695.2 | 43680.9 | 12199.4 | 3956.9 | 2800.0 | 14057.9 |
| green degree (gd/h) | -141009.9 | -130350.4 | -2824.5 | -2226.8 | -1803.1 | -3805.0 |
| stream composition (mass fraction) | | | | | | |
| O ₂ | 0.0026 | 0 | 0.0162 | 0 | 0 | 0 |
| H ₂ O | 0.0344 | 0 | 0.0043 | 0.5864 | 0.0921 | 0 |
| MAL | 0.0258 | 0 | 0.0049 | 0.2421 | 0.3273 | 0.0030 |
| CH ₄ O | 0.5265 | 0.8807 | 0.0662 | 0.1676 | 0.1579 | 0 |
| IB | 0.0002 | 0 | 0.0014 | 0 | 0 | 0 |
| MMA | 0.2663 | 0.1192 | 0 | 0.0038 | 0.4227 | 0.9970 |
| C ₂ H ₄ O ₂ | 0 | 0 | 0 | 0 | 0 | 0 |
| C ₃ H ₆ O | 0 | 0 | 0 | 0 | 0 | 0 |
| CH ₂ O | 0 | 0 | 0 | 0 | 0 | 0 |
| MAA | 0 | 0 | 0 | 0 | 0 | 0 |
| C ₄ H ₁₀ | 0.0002 | 0 | 0.0010 | 0 | 0 | 0 |
| N ₂ | 0.1407 | 0 | 0.8843 | 0 | 0 | 0 |
| CO | 0 | 0 | 0.0001 | 0 | 0 | 0 |
| CO ₂ | 0.003 | 0 | 0.0216 | 0 | 0 | 0 |

^a MAL, methacrolein; CH₄O, methanol; IB, isobutylene; MAA, methacrylic acid; MMA, methyl methacrylate; C₄H₁₀, butane.

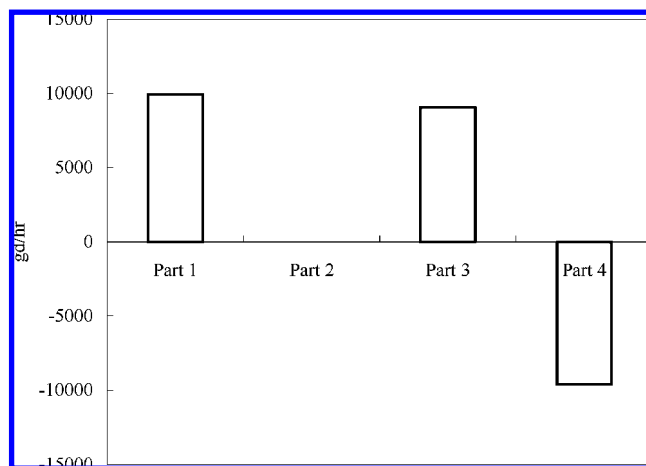


Figure 5. Green degree production values of the four parts of the MMA production process by the *i*-C4 route.

4. Conclusions

In this work, the green degree method is proposed to quantitatively evaluate and analyze the environmental impact of a chemical process. Detailed definitions and calculation formulas for the green degree values of a substance, a mixture, and a unit (process) are illustrated. Because the green degree value integrates nine environmental impact categories and can be combined with rigorous chemical process simulation technology, it is more comprehensive and helpful for assessing and understanding the environmental performance of complex chemical processes. Three industrial applications were discussed here: solvent screening, product synthesis route screening, and process environmental impact evaluation of the MMA process with the *i*-C4 route. The results show that the proposed method provides a useful tool for chemical process design for environment (DfE) efforts.

Chemical processes are very complicated systems. In the past, material and energy integration technologies have been developed for optimizing the mass and energy utilization, which impelled the transformation of the chemical industry from a simple resource utilization pattern to resource saving, reuse, and

recycling. We believe that integrating green degree values with material and energy flows in a process will make the current process design approach much greener and more sustainable. It also provides a quantitative tool for evaluating environmental impacts to optimize and integrate chemical processes with respect to the overall life cycles of products, as well as a process for designing new processes and retrofitting existing ones.

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