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Energy-Efficient Routes for the Production of Gasoline from Biogas and Pyrolysis Oil—Process Design and Life-Cycle Assessment

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ABSTRACT: Two novel routes for the production of gasoline from pyrolysis oil (from timber pine) and biogas (from ley grass) are simulated, followed by a cradle-to-gate life-cycle assessment of the two production routes. The main aim of this work is to conduct a holistic evaluation of the proposed routes and benchmark them against the conventional route of producing gasoline from natural gas. A previously commercialized method of synthesizing gasoline involves conversion of natural gas to syngas, which is further converted to methanol, and then as a last step, the methanol is converted to gasoline. In the new proposed routes, the syngas production step is different; syngas is produced from a mixture of pyrolysis oil and biogas in the following two ways: (i) autothermal reforming of pyrolysis oil and biogas, in which there are two reactions in one reactor (ATR) and (ii) steam reforming of pyrolysis oil and catalytic partial oxidation of biogas, in which there are separated but thermally coupled reactions and reactors (CR). The other two steps to produce methanol from syngas, and gasoline from methanol, remain the same. The purpose of this simulation is to have an ex-ante comparison of the performance of the new routes against a reference, in terms of energy and sustainability. Thus, at this stage of simulations, nonrigorous, equilibrium-based models have been used for reactors, which will give the best case conversions for each step. For the conventional production route, conversion and yield data available in the literature have been used, wherever available. The results of the process design showed that the second method (separate, but thermally coupled reforming) has a carbon efficiency of 0.53, compared to the conventional route (0.48), as well as the first route (0.40). The life-cycle assessment results revealed that the newly proposed processes have a clear advantage over the conventional process in some categories, particularly the global warming potential and primary energy demand; but there are also some in which the conventional route fares better, such as the human toxicity potential and the categories related to land-use change such as biotic production potential and the groundwater resistance indicator. The results confirmed that even though using biomass such as timber pine as raw material does result in reduced greenhouse gas emissions, the activities associated with biomass, such as cultivation and harvesting, contribute to the environmental footprint, particularly the land use change categories. This gives an impetus to investigate the potential of agricultural, forest, or even food waste, which would be likely to have a substantially lower impact on the environment. Moreover, it could be seen that the source of electricity used in the process has a major impact on the environmental performance.

1. INTRODUCTION

Most of the world’s gasoline today is produced via crude oil distillation and subsequent refining.¹ Though popular, companies worldwide are exploring alternate methods to produce gasoline and other liquid fuels. The main drivers for this are an abundant availability of gas and coal, monetary gains involved in exploiting new reserves, the need to ensure a continuous supply of energy for a rapidly growing population, and an increasing call for cleaner fuels.²⁻⁴ Moreover, reserves of crude oil are finite, and will be exhausted in the future.⁴⁻⁵ Thus, other production routes such as natural gas-to-liquid fuels (GTL) and coal-to-liquid fuels (CTL) techniques have been investigated in detail, and have even been implemented in the industry.⁶⁻⁷ Even so, coal and natural gas are nonrenewable resources, and even with state-of-the-art technology, they have a negative impact on the environment in their production and use phases.⁸ Governments around the world (and especially in the European Union) are investing in developing new technology to reduce the environmental footprint of anthropogenic activities, and making them part of public policy.⁹ Thus, of late, there has been an increased focus within the EU on the development of cleaner ways to produce liquid fuels, by using biomass-based products as the starting material.¹⁰⁻¹¹

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As mentioned above, the key motivation behind exploring biomass as raw material is the environmental benefit associated with its use. Biomass is a carbon-neutral resource, and can help negate the harmful effects associated with the utilization of fuels for transport, cooking, or heating. Whether biomass is indeed a viable solution to problems related to sustainability and climate change needs to be looked into by employing an established method to quantify these benefits (or reduction in the ill-effects), compared to fossil fuels.

In this context, life-cycle assessment (LCA) is gaining popularity as a tool to assess the environmental impacts of different processes in a number of industries. The LCA is defined by the ISO 14040 as “the compilation and evaluation of the inputs, outputs, and potential environmental impacts of a product system throughout its life cycle.”12 The environmental burden of a product system can be manifested in a number of ways, such as land use changes, emissions to the air, soil, and water, global warming potential, nonrenewable primary energy demand, and so on. The LCA is a way to measure these impacts, and identify which parts of the process contribute to these impacts. LCA is being used in a wide range of research areas in chemistry and chemical engineering; these include pharmaceuticals, bulk chemicals, and specialty chemicals, as well as novel reactor designs.13,14

There are a multitude of biomass-based processes and products that have been subjected to life-cycle assessment studies, as evidenced in the literature.15,16 All the different phases in the entire biofuel chain—from the availability and growth of raw material, harvesting, and transport to the production of fuel, use, and disposal—can be studied in an LCA. Each phase contributes to the total impact of that product over its lifetime.

Looking specifically at case studies involving biomass, most studies include (or sometimes only focus) on the use phase of a product, for example, studies on the use of biodiesel and bioethanol in automobiles, and their impact on the environment.17–18 Since the system boundaries under study are different in each of these cases, it is not always possible to generalize and conclude about the sustainability of all biomass-related studies. However, it is still worth studying them, to see what the general consensus is about biomass-based fuels/chemicals.

Numerous studies involving the production and use of biofuels have been reported in literature.19,20 For example, a study on the production and use of gasoline and diesel via fast pyrolysis and hydroprocessing starting with forest residue is compared with that of conventional gasoline.20 By carrying out a Monte Carlo uncertainty analysis, the study found that greenhouse gas (GHG) emissions as well as the net energy value (NEV) were lower for the pyrolysis gasoline and diesel than for conventional gasoline. Moreover, the study also pointed out that even better GHG results can be obtained if the electricity and hydrogen used for the production process of pyrolysis gasoline and diesel are derived from biomass.19

Another similar study compared the life cycles of alternative automobile fuels such as gasoline, diesel, compressed natural gas (CNG), and ethanol (C2H5OH)-fueld internal combustion engine (ICE) automobiles. It was concluded that the bioethanol offers reduction in GHG emissions compared to the other options; also ethanol from woody or herbaceous biomass is more sustainable than using food crops.20 However, from an economic perspective, CNG was the best choice, and also offered lower emissions compared to gasoline and diesel. Some studies also focus solely on investigating the cultivation and cropping of different kinds of biomass. For example, a comparative study of the environmental performance of three systems was conducted; the cultivation of the poplar bioenergy system, Ethiopian mustard bioenergy system, and extraction of natural gas.21 It was found that the poplar bioenergy system was much more energy efficient that the natural gas exploitation process, as well as the Ethiopian mustard bioenergy system.

Similar results were reported in a study that compared two routes for producing 1,4-butandiol, one from conventional hydrocarbon feedstock to produce formaldehyde and acetylene and then finally 1,4-butandiol, and the other alternative route using biomass, where glucose from corn is subjected to fermentation to give the final product.22 Here, only the raw material procurement, and production phases are considered; the use and recycle phases are excluded. Once again, the results showed that the biomass-based process performs better than the hydrocarbon-based process from the energy consumption as well as environmental points of view. However, in terms of use of fuel resource consumption (based on the Life Cycle Inventory), the alternative route was higher, which was attributed to the greater use of electricity from conventional sources in the production process.22 The paper did not give a concrete answer as to which process was more environmentally sound, but suggested possible changes to better the alternate process.

Another work focusing on the process technology part of a biomass-based process has been reported.23 Here, a new route to produce diesel from feedstocks such as soybean, palm, and rapeseed oils (called green diesel) is compared with biodiesel (also from the same biomass feedstocks mentioned above) and petroleum diesel. Once again, it was concluded that for all cases, the green diesel had a better GHG emission profile compared to the other two types of diesel. The energy consumption for the green diesel process was lower than the biodiesel if the hydrogen for the process was produced internally rather than sourcing it externally.23

An interesting case study was conducted to look at the production of bioethanol (along with bioenergy and biochemicals) in a biorefinery, using switchgrass, a lignocellulosic crop, as the raw material.24 A comparison of the results with a similar fossil-fuel based system showed that the biorefinery did reduce GHG emissions by 79% and nonrenewable energy use by 80%. However, it also concluded that impacts were higher for the biorefinery than the fossil-fuel based system in the categories of acidification and eutrophication, mainly due to land use effects, fertilizer production, and transport.

This last finding is echoed in a review of bioethanol LCA studies.17 This comprehensive analysis of LCAs of bioethanol concludes that, from the GHG emission and energy points of view, bioethanols performed consistently better than conventional fuels. However, apart from these parameters, the performance of the bioethanol systems for other categories such as acidification, human toxicity, and ecotoxicology were mixed, and in fact, favored the fossil fuel systems.17 This also depended on the type of biomass used, and the system boundaries of the study, since a cradle-to-grave analysis gives a more comprehensive overview of the impacts of these fuels. Similar results have been reported in a few other studies.25,26

Another critical aspect of biofuels, as well as other sectors such as industry and mining and so on, is the reported effect of land use changes associated with the use of the land for that particular activity.27,28 However, since the cultivation of energy
The use of biofuel in the long run. Moreover, when land that has potential to reverse the greenhouse gas savings achieved by the cascading effects of feedstock for biofuels, it results in a series of changes, such as the biodiversity, soil quality, and the biotic activity. The soil in these forests and grasslands acts as a sink for carbon, which is released into the air when the land is cleared for production of biofuel feedstocks. This has the potential to reverse the greenhouse gas savings achieved by the use of the biofuel in the long run. Moreover, when land that was used to produce a certain kind of crop is diverted for the production of feedstock for biofuels, it results in a series of cascading effects, which results in more virgin land being cleared to maintain the production level of the displaced crop. This results in the release of even more carbon. Thus, the carbon balance and GHG savings calculated must reflect the changes associated with land use. Moreover, it is important to look at the other sustainability criteria associated with land use changes, such as the biodiversity, soil quality, and the biotic production potential.

Thus, to summarize, literature has shown that significant carbon benefits can be accrued by shifting to biomass-based processes and products. However, biomass-based fuels and products do not always present an environmentally favorable picture, and require deeper analysis of the effects of feedstock production and product use phases.

In this work, we shall present the results of an ex-ante life-cycle assessment for only the production phase of a new process to produce gasoline from biogas and pyrolysis oil. First, two new production routes and a conventional process (to benchmark the new routes) are simulated in the software Aspen Plus V8.6. The purpose of this simulation is to have an ex-ante comparison of the performance of the new routes against a reference, in terms of energy and sustainability. Thus, at this stage of simulations, nonrigorous, equilibrium-based models have been used for reactors, which will give the best case conversions for each step. For the conventional production route, conversion and yield data available in literature have been used, wherever available. In all cases, the separator models used are simple (typically, flash columns where one can specify the fraction of the desired component in each stream). Next, heat integration is achieved for each case carrying out a pinch analysis. Lastly, the energy and mass flows from the above simulations are transferred to the LCA software GaBi Professional, and the resulting impacts are studied and discussed in detail. The paper first looks at the methodology of the above-mentioned steps, and then the results are presented and discussed.

## 2. METHODOLOGY

### 2.1. Process Simulations and Heat Integration.

As stated above, the BIOGO project explores a different route to produce gasoline. Instead of following the conventional methanol-to-gasoline (MtG) route, it looks at gasoline production from biogas and pyrolysis oil.

The conventional route is as shown in Figure 1 and will be referred to as the “Base” case henceforth. It is a process already established in the industry, and is quite complex in design. In this work, this process is simulated so that it can serve as a benchmark for the BIOGO processes and is not intended for deeper process optimization of the existing industrial process. Consequently, the design of the process serves to provide mass and energy balances for the LCA.

Here, the natural gas is fed into the autothermal reactor, where steam and oxygen are also added in a specified ratio. The syngas produced is then adjusted, and sent for methanol synthesis and then further to the gasoline production step.

The BIOGO routes use pyrolysis oil and biogas as the starting material. Pyrolysis oil is the liquid fraction produced by fast pyrolysis, a quick, thermal decomposition of organic matter, at moderate temperatures in the absence of oxygen. The pyrolysis oil is typically made up of a number of oxygenated organic compounds—sometimes up to 400 compounds; a mixture of aldehydes, ketones, carboxylic acids, esters and aromatics, and the composition of the pyrolysis oil varies with the kind of biomass feedstock, reactor type, residence time, etc. Thus, in order to simplify the simulation, model compounds have been used to represent the pyrolysis oil; this method is commonly adopted in the literature. On the basis of input from partners, a pyrolysis oil composition of 25% acetic acid, 15% acetone, 15% anisol, 15% guaiacol, 15% tetrahydrofuran (THF), and 15% water has been used. However, it must be noted that the composition of the bio-oil depends strongly on the feedstock from which it is sourced. Consequently, the composition of the bio-oil affects the composition of the syngas; for example, an experimental study of fast-pyrolysis of different model compounds showed that acids and oxygenated aromatics were easily converted to hydrogen and carbon oxides at a temperature of 650 °C, with a S/C ratio between 3 and 6. However, under the same conditions, sugars such as glucose and xylose were difficult to convert to syngas, and required a much higher S/C ratio.

Biogas is produced by anaerobic digestion of a variety of raw material—food waste, agricultural waste, energy crops, animal manure, sludge from wastewater treatment plants, and so on.

The composition of biogas also varies with the kind of feed and production times, but a typical composition of biogas could be 50–85% CH₄, 20–35% CO₂, and the rest is a mixture of H₂, N₂, and H₂O. Thus, in this work, we assume a biogas composition of 70% CH₄ and 30% CO₂.
The proposed routes are as follows:

(i) ATR: Autothermal reforming of pyrolysis oil and biogas. As shown in Figure 2, the pyrolysis oil and biogas are subjected to autothermal reforming in a single reactor, with the addition of steam and oxygen. The idea is that the two feed materials get reformed such that no external energy needs to be supplied to the reactor. The processes downstream of this step remain the same as shown in the Base case.

(ii) CR (coupled reforming). Steam reforming of pyrolysis oil and catalytic partial oxidation of biogas: separate but coupled reactions.

CR adopts a different method for the production of syngas, as depicted in Figure 3. Here, the steam reforming of pyrolysis oil (an endothermic reaction) and catalytic partial oxidation of biogas (an exothermic reaction) are coupled, such that they balance each other thermally. Thus, this step will need no external energy input. Once again, the remaining steps will remain unchanged.

To compare the two new processes with the Base case in terms of efficiency of performance, the carbon efficiency is calculated and compared in each case. Carbon efficiency is defined as:

\[
\text{carbon efficiency} = \frac{\text{amount of carbon in product}}{\text{total carbon present in reactants}} \times 100
\]

As mentioned earlier, this simulation aims to carry out an extensive comparison of the performance of the new cases against the conventional route. Also, catalyst selection and kinetic studies are still in progress for the new processes, which will later be updated in the model. Thus, the simulations presented here are not rigorous and use equilibrium-based models. Thus, the estimates of energy consumption calculated by the software will be of the same level of accuracy for all cases. This is a key point for the LCA, since the ILCD Handbook states that, for comparisons, the inventory data that is used for the analysis must possess approximately the same degree of accuracy and precision.\(^45\) This means that the level or degree of detailing in all the simulations should be similar.

Since most of the components are hydrocarbons, the Peng–Robinson model has been used as the base property method (as suggested by Aspen Plus). For the methanol synthesis step, the Soave–Redlich–Kwong property method is reported to be suitable.\(^47\)

All three cases are simulated for a capacity of 30 ktons/year. This is an average value, based on capacities of the latest, state-of-the-art, planned biomass-to-fuels plants reported in press. These include the small-scale, nonfood biomass-to-fuels biorefinery planned by CoolPlanet Energy Systems in Alexandria, Louisiana (the United States)\(^48\) and a modified fluid catalytic cracking plant that transforms biomass to fuel (FCC) by KiOR in Columbus, Mississippi (the United States)\(^49\).

Next, heat integration is carried out for the above process. Heat management or integration involves exploring opportunities to integrate the generated heat within the process itself, and reducing the consumption of utilities. The new cases already have heat integration as a part of the design, since the syngas generation step in the ATR case does not require supply of any additional energy, and the CR case has the catalytic partial oxidation of biogas exchanging heat with the steam reforming of pyrolysis oil. However, there is further scope for energy savings within the process, one of which is the technique of “pinch analysis” (developed by Linnhoff in the 1970s) which has been widely recognized as one of the most effective methods of heat integration.\(^50\) It involves the design of a heat exchanger network (HEN) that exchanges heat between process streams as far as possible, and the deficit (either heating or cooling) can then be supplied by utilities. Detailed information about the heat exchanger network and pinch analysis can be found in the literature.\(^51\)

Pinch analysis has been used previously as reported in the literature to achieve heat integration for chemical processes. The main purpose of the pinch analysis here is to minimize utility consumption, which also naturally lowers operating costs. Thus, the three cases developed have been optimized for utility consumption by carrying out a pinch analysis. The final utility values are then plugged into the LCA to see their impact.

The software program Aspen Energy Analyzer V8.6 has been used to carry out the pinch analysis. For the detailed procedure, the reader is referred to the Supporting Information.

2.2. Life-Cycle Assessment (LCA) Methodology. This section discusses the methodology adopted for the LCA study. The governing document for the LCA methodology is the set of standards for LCA published by the International Standards Organisation (ISO), ISO 14040/44. On the basis of these standards, the Institute for Environment and Sustainability in the European Commission Joint Research Centre (JRC), in cooperation with the Environment DG has developed the International Reference Life Cycle Data System (ILCD) Handbook, as a comprehensive guide to LCA studies. It provides a detailed discussion of the LCA methodology, and a common basis for consistent, robust, and quality-assured life cycle data and studies.

The software used for this LCA study is the GaBi software (along with the GaBi Professional Database), developed by thinkstep, Germany. The documentation of the GaBi database is in-line with the ILCD Handbook.

The LCA methodology can be described as an iterative approach with the followings steps: goal and scope definition, inventory analysis, impact assessment, and improvement assessment steps.\(^52\) Each of these steps is applied and discussed henceforth. The following sections discuss the approach adopted for the LCA.
2.2.1. Goal and Scope Definition. The goal of this LCA is to evaluate and compare the impacts generated and resources consumed in the three cases, which are designed to produce gasoline as the main product, with a number of other hydrocarbons as byproduct. The study aims to investigate the effects of using biomass-based raw material (ATR and CR cases), in lieu of natural gas (Base case), as well as the efficiency of the process design.

2.2.2. System Boundaries. The LCA study presented here is a “cradle-to-factory gate” analysis, which starts with the raw material required for the process and stops at the production step. The system boundaries can be represented diagrammatically, as can be seen for the Base case and the ATR and CR cases in Figure 4. The Base case as well as the ATR and CR cases include all the processes shown in the process flowsheets. The Base case starts with the autothermal reforming of natural gas, while the other two cases have the biogas and pyrolysis oil as their feed. The LCA of the Base case includes the upstream processes involved in extracting and processing the natural gas. The input flows are depicted as flowing into their respective units; for example, the natural gas/biogas/pyrolysis oil, steam, and oxygen enter the autothermal reformer/coupled reformer, while the electricity goes to the compressors, and cooling and heating to their respective process units. Waste streams flow out from the separators, while the final product (gasoline) flows out, along with the remaining hydrocarbons.

The functional unit is specified here, to be 1 kg of gasoline produced. Thus, all mass and energy flows are scaled down to 1 kg of gasoline.

It must be noted that the LCA does not include the manufacturing of the equipment in the plant such as reactors and heat exchangers, or the transport of raw materials. Also, the inventory associated with the manufacture of catalysts and their use has not been included in this study.

2.2.3. Quality of Data. The quality of data is an important point to be noted while carrying out the LCA.52 The data quality depends on two main factors: the mass and energy flows into the system, and the inventory data.53 The mass and energy flows are obtained from the Aspen simulations, which are based on literature values, and design considerations; thus, they can be said to be of high quality. The inventory data depends on the database employed, and a list of the units used from the GaBi Database have been provided in Table 1. Additionally, some assumptions have been made in the inventory data, as given below:

- The type of biomass used to produce pyrolysis oil is timber pine, and the data for the cultivation, harvesting,
and collection of timber pine is available as a built-in unit in the GaBi Professional Database. However, the energy input for the actual production of pyrolysis oil from the timber pine is not available. Thus, this value has been obtained from literature to be 1.9 MJ/kg of pine.\(^{64}\)

- The biogas can be produced from a wide range of biomass sources, such as agricultural waste, energy crops, and food waste. However, there is no in-built unit in the GaBi Professional Database for the growth and cultivation of the associated energy crops, or the upstream activities associated with agricultural and food waste. Therefore, the flows associated with the cultivation of the biomass for biogas production has been excluded from this analysis. However, the energy for the harvesting of certain kinds of biomass, as well as the associated energy for the actual production step is available in the literature. In this work, the biomass source is assumed to be ley grass,\(^{55}\) and the energy for harvesting is 2.72 GJ/ton of dry biomass, and the thermal energy for production of biogas is 250 MJ/ton of biogas, while the electricity required is 33 MJ/ton of biogas.\(^{55}\)

- The majority of the inventory data are applicable to the European Union (EU-27). In the case of timber pine, EU data was not available, so data from Germany has been used.

- The cooling utility used here is tap water, purified after water treatment. Since cooling water is usually a closed-loop system in large plants, a fixed amount of water is circulated constantly. Some amount of water is lost continuously, which needs to be replenished. This is the makeup water, and only the amount of makeup water needs to be considered in this study. Thus, the amount of makeup water needed per kilogram of gasoline is calculated based on the total cooling water requirement. Evaporation losses are 1% of the circulation for every 100 °F of cooling range (that is, 1% loss for every 100 °F of cooling required), windage or drift losses of mechanical draft towers are 0.1−0.3%, and blowdown of 0.5−3.0% of the circulation is necessary to prevent excessive salt buildup.\(^{56,57}\)

Further details regarding the LCA methodology, such as allocation, inventory analysis, and impact categories can be found in the Supporting Information.

The forthcoming sections will present the results of the Life Cycle Impact Assessment (LCIA) and discuss the findings in detail.

3. RESULTS AND DISCUSSION

3.1. Process Simulation and Heat Integration Results.

3.1.1. The Conventional Process (Base Case). In the conventional synthetic gasoline process, the starting material could either be natural gas or coal. In this case, we use natural gas as the starting material, as done by Mobil in the Mobil MTG process in 1978 in New Zealand.\(^{57}\) In the original MTG process, the first step is achieved by steam reforming the natural gas. However, steam reforming is an energy-intensive and expensive step. Since the 1970s, there has been significant progress in syngas synthesis, and nowadays, the most popular method for the synthesis of syngas is autothermal reforming.\(^{58}\) This kind of reactor has both the steam reforming of methane (an endothermic reaction) as well as the noncatalytic partial oxidation (an exothermic reaction) taking place.\(^{59}\) Therefore, this reactor does not need to be supplied by any external energy (heating or cooling), since the reactions taking place in the reactor supply energy to each other. Thus, in the conventional route simulated in this work, syngas generation is achieved by autothermal reforming.

In the first step, natural gas, steam, and oxygen are compressed to 30 bar in multistage compressors (with interstage cooling). Multistage compressors are used since compressing to 30 bar raises the exit temperature of the gas beyond practical limits. Thus, it is recommended to maintain the exit temperature below 200 °C.\(^{59} \) The gases are then heated to 700 °C and sent to the ATR reactor, which is maintained at 800 °C and 30 bar.\(^{61}\) The reactor is a Gribb’s reactor with the following reaction set:\(^{62}\)

\[
\begin{align*}
CH_4 + 0.5O_2 & \rightarrow CO + 2H_2 \\
CH_4 + H_2O & \rightarrow CO + 3H_2 \\
CO + H_2O & \rightarrow CO_2 + H_2 \\
CH_2O & \rightarrow CH_2OH + H_2O \\
CO + 2H_2 & \rightarrow CH_2OH
\end{align*}
\]

The heat duty of the ATR reactor is maintained at zero, and the flow rate of the oxygen stream is manipulated to maintain the outlet temperature of the product gas at 1020 °C.\(^{53}\)

The outlet syngas is cooled and sent to a component separator (where the outlet flows can be specified) which adjusts the composition of the syngas. A ratio of \((H_2 - CO_2)/(CO + CO_2)\), called the molar ratio \(M\), that is slightly greater than 2, must be achieved. Some percentage of \(CO_2\) and some \(H_2\) is removed to obtain an \(M\) approximately equal to 2.2. This condition is required for a good methanol yield.\(^{58}\) The adjusted syngas is then compressed in a multistage compressor to 70 bar, heated to 250 °C, and sent to the methanol reactor.

The methanol synthesis is generally carried out at pressures ranging from 50 to 100 bar, temperatures are around 250–280 °C. Thus, the reactor is modeled as a stoichiometric reactor at 275 °C and 70 bar with the following reactions:

\[
\begin{align*}
CO_2 + 3H_2 & \rightarrow CH_3OH + H_2O \\
CO + 2H_2 & \rightarrow CH_3OH
\end{align*}
\]

The conversion data for \(CO\) and \(CO_2\) at equilibrium are specified in the literature for this temperature and pressure to be 0.506 and 0.059, respectively.\(^{64}\) The product stream is expanded, cooled to 110 °C, and sent to a component separator, where the unreacted syngas is separated and recycled back to the methanol reactor.

The separated methanol is then sent to the gasoline reactor, which is operated at 20 bar and 360 °C.\(^{65}\) The methanol is also heated to 360 °C and sent to the gasoline reactor. Industrially, the methanol to gasoline (or MTG) reaction is a two-step reaction carried out in two reactors in series, which proceeds via the production of DME as an intermediate. It gives a product yield of 43% hydrocarbons and 57% water. The hydrocarbon product is a mixture of olefins, paraffins, and aromatics from \(C_2-C_{12}\), of which only the \(C_5\) and higher compounds constitute gasoline. The reaction mechanism can be approximated as follows:\(^{66,31}\)

Step 1:

\[
2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O
\]

Step 2:

\[
CH_2OH, CH_3OCH_3 \rightarrow light \text{olefins} + H_2O
\]
light olefins → C₃ + olefins
paraffins
C₃ + olefins → naphthenes
gasoline
aromatics

Here, for the sake of simplicity, the entire methanol to gasoline reaction is simulated as a single step in one reactor. Since the reaction is a complex one with numerous products, and no documented conversion data is available for every single reaction, the MTG reactor is simulated as a yield reactor, using the product distributions of the product stream available in literature. The gasoline fractions of the hydrocarbon product are then separated using a split fraction model.

The overall carbon efficiency is calculated for the Base case using the formula mentioned earlier. The value for the Base case is 0.48. The flowsheet for the Base case can be seen in Figure 5.

The heat integration by pinch analysis for the Base case resulted in a reduction of heating utility from 14.12 MW to 0 MW, while the cooling utility reduced from 19.24 MW to 5.12 MW. The detailed results of the pinch analysis are tabulated in the Supporting Information.

3.1.2. The New Processes—ATR and CR. In the two new proposed routes for the production of gasoline from biogas and pyrolysis oil, the key difference is the method of production of syngas from the raw material. The first process is the autothermal reforming of biogas and pyrolysis oil (called ATR), similar to the autothermal reforming of natural gas. The second process involves the endothermic steam reforming of the pyrolysis oil, and exothermic catalytic partial oxidation of biogas, carried out in a coupled heat exchanger (called CR). In this second method, the two reactions will exchange heat with each other, so no extra energy needs to be supplied to the reactor. The flowsheets for both cases are shown in Figure 6.

I. ATR Case: Autothermal Reforming of Biogas and Pyrolysis Oil. An equimolar feed of biogas and pyrolysis oil is used in the first step, which is the generation of syngas. The raw material, along with some steam and oxygen, are heated to 800 °C, and compressed and sent to the autothermal reactor.
Hence, the syngas generation step is carried out at 1 bar and 800 °C. The steam to carbon ratio is maintained at 4 (using a design specification) since a high S/C ratio is recommended for such operations to avoid coking in the reactor. The O₂/C is adjusted to maintain the product gas temperature at 800 °C. Since pyrolysis oil is such a complex mixture of different compounds, the autothermal reactor is simulated as a Gibbs reactor, where the composition of the product stream is predicted, based on thermodynamic equilibrium.

The syngas obtained from the autothermal reactor contains a high amount of CO₂, and it is not advisable to remove all the CO₂ to adjust the syngas composition, since it results in a loss of valuable carbon. Thus, a reverse water gas shift reactor (RWGS) is added after the syngas generation step, to convert the excess CO₂ to CO. The RWGS reactor is simulated as an equilibrium reactor, maintained at 620 °C and 1 bar, with the following endothermic reaction:

\[ \text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad (8) \]

The product from the RWGS reactor still needs to be adjusted to achieve the \((\text{H}_2 - \text{CO}_2)/(\text{CO} + \text{CO}_2)\) ratio of ~2.04. Thus, a component separator is added to adjust the syngas composition. After this step, the syngas is compressed to 70 bar and sent to the methanol reactor. The methanol reactor is simulated as a predictive equilibrium reactor, with the same reaction set (eqs 4 and 5) as mentioned in the conventional process. The product gas is then expanded to 1 bar, cooled to 150 °C, and sent to a component separator which separates the methanol from the unreacted syngas. Also, the methanol reactor generates some water and CO₂, which does not contribute to the methanol synthesis, but just builds up in the recycle loop. The CO₂ and water are also removed in this step. The rest of the recycle gas is then compressed to 70 bar, heated, and routed back to the methanol reactor.

The separated methanol is compressed to 20 bar, heated to 360 °C, and sent ahead to the gasoline reactor. It is not possible to simulate the gasoline reactor as a predictive reactor, as there is no fixed reaction set for this reaction. Moreover, this is not an equilibrium reaction, and the product distribution cannot be estimated by this method. Thus, we use the same yield reactor as used for the Base case, with the mechanism specified in eqs 6 and 7, and product distributions from literature. The gasoline fractions of the hydrocarbon product are then cooled and separated using a split fraction model.

The carbon efficiency obtained for the CR case is 0.536. The heat integration by pinch analysis for the CR case resulted in a reduction of heating utility from 20.85 MW to 1.83 MW, while the cooling utility reduced from 43.91 MW to 5.69 MW. The detailed results of the pinch analysis are tabulated in the Supporting Information.

### 3.1.3. Discussion

The difference in the carbon efficiencies can be attributed to the difference in the behavior of the ATR and CR processes to produce syngas. For the ATR process, the heat output over the reactor is fixed as zero, which leads to an increase in the outlet temperature of the product. Thus, the amount of bio-oil, biogas, and oxygen is varied until the desired temperature of 800 °C is reached for the outlet temperature. This gives a certain syngas composition (mole fractions: \(\text{CO} = 0.079, \text{CO}_2 = 0.119, \text{H}_2\text{O} = 0.478, \text{H}_2 = 0.324\)) for the ATR case. Here, we can see that the conversion to CO₂ is more than that to CO (probably due to the influence of the WGS reaction in the autothermal reformer).

On the other hand, in the CR case, the two reactors have their temperatures fixed at 800 °C, and the flow rates of the bio-oil and biogas are adjusted to achieve thermal coupling between the two reactors. The steam/carbon ratio for the steam reforming of pyrolysis oil is fixed at 4, while the oxygen flow to the partial oxidation of biogas is adjusted such that the oxygen/carbon ratio = 0.5. This results in a different composition of syngas (\(\text{CH}_4 = 0.0029, \text{CO} = 0.29, \text{CO}_2 = 0.065, \text{H}_2\text{O} = 0.17, \text{H}_2 = 0.46\)).

Thus, the CR case converts more of the inlet carbon to CO, which is essential for methanol production. This difference in
syngas composition determines how much of CO₂ and CO need to be removed in each process, to maintain the ratio of \((H₂ - CO₂)/(CO + CO₂)\) slightly higher than 2. This is where carbon is lost from the process and is different for the three cases. This also affects the next step, methanol production, which is determined by equilibrium. A little of the unreacted carbon from the product stream of the methanol reactor gets purged, while the rest gets recycled. Only the carbon that was converted to methanol is available for the production of gasoline. Thus, we have a higher carbon efficiency for the CR case, as compared to the ATR case.

It must be mentioned here that the ratio of ley grass and timber depends on the amount of biogas and bio-oil to be produced. For example, in the CR case, the flow rates of the biogas and bio-oil have been set based on the condition for thermal coupling of the steam reforming of the bio-oil, and the partial oxidation of the biogas, at 800 °C. That is, the amount of biogas and bio-oil are varied at 800 °C until the two reactions balance each other. This determines the amount of ley grass and timber pine required, based on energy yields from literature. For the ATR case, this comes to 5672.57 kg/h of ley grass and 19282.83 kg/h of timber pine, while for the CR case, it is 25845.08 kg/h and 2956.67 kg/h of ley grass and timber pine, respectively. For detailed calculations, please refer to the Supporting Information.

### 3.2. Life-Cycle Assessment Results

#### 3.2.1. Comparison of Environmental Profiles of the Base Case and ATR and CR Cases, per Impact Category

The graphs below present the results of the LCA for the ATR case (autothermal reforming of pyrolysis oil and biogas) and CR case (separate, but coupled reforming of pyrolysis oil, and catalytic partial oxidation of biogas), compared to the Base case (conventional process of gasoline from natural gas). The results have been presented as impacts/kg of gasoline produced. As mentioned earlier, allocation has been carried out in all three cases, since a number of byproducts are also formed.

The environmental profiles of the three cases have been described in detail for the CML categories of global warming potential (GWP), acidification potential (AP), and human toxicity potential (HTP). A single plot providing an overall comparison of all CML categories for the three cases has also been described.

Land use change impacts have also been investigated through categories such as land occupation and transformation indicators, biotic production (occupation and transformation), and groundwater replenishment indicator (occupation and transformation). Land use change impacts are studied by considering the impacts in two phases: occupation (as when the land is actually in use) and transformation (as the permanent effect on the land due to its use for a particular activity).

The results of the GWP, as seen in Figure 7, show that the two new processes fare better than the Base case. This is mainly due to the use of biomass (timber pine) as the feed, instead of natural gas. The cultivation of timber pine results in a negative GWP, which lowers the overall value (the overall value is shown on the right of each case). Out of the two new processes, the ATR case (autothermal reforming of pyrolysis oil and biogas) performs better than the CR case. This can be attributed to the fact that more pyrolysis oil is used in the ATR case (compared to the CR case), which means more timber pine is required, and leads to a larger negative value. Even so, as seen from the figure below, even without the positive impact of the use of biomass, the GWP from other categories is still lower than that of the Base case. For the Base case, the natural gas use has considerable impact, while the waste streams in all three cases also contribute significantly to the GWP; this is due to removal of CO₂ to adjust the syngas composition in the process.

It must be noted that the CO₂ equiv values reported here include the effects of land use changes associated with the growth of the timber. Thus, even with the carbon loss associated with the clearing of the land for biomass, the ATR and CR processes have a better footprint than the Base case.

On the other hand, the acidification potential, which can be seen in Figure 8, shows that the performance of all three cases is almost the same. The main subunit contributing the most to
all cases is the unit “Electricity for the compressors”, which is comparable in all three. The electricity in all three cases comes from the grid, which is a mix of all sources of electricity production. This mix is dominated by nuclear energy, followed by natural gas, coal, and waste. Power plants contribute significantly to SO\(_2\) and NO\(_x\) emissions, \(^{68}\) which lead to such a high influence from them in the AP category. For the Base case, the natural gas is the biggest contributor; this shows that the extraction of natural gas consumes resource that give out considerable emissions which impact the acidification potential. For ATR, the cultivation and harvesting of timber pine makes a large impact. This can be attributed to the diesel fuel needed to transport the timber to the saw mill, and the power input required from the grid to run the saw mill. These steps draw on resources which impact the overall emissions of the process. Similarly, for CR, the energy for harvesting the ley grass comes from diesel, which runs the vehicles. This diesel comes from crude oil distillation, which is a highly energy-intensive process in itself, and results in significant emissions.

On the other hand, the results of the human toxicity potential (refer to Figure 9), show that the Base case has a more favorable profile. The HTP reflects the effect of certain substances that can affect human health. The chief contributors in the new processes (apart from the electricity consumption, which is once again comparable) are the biomass-related inputs, that is, the cultivation and harvesting of timber pine, and the energy for harvesting ley grass for biogas production. As mentioned earlier, these steps involve use of electric power from the grid, as well as consumption of diesel. Thus, these steps contribute measurably to the HTP. Also, the oxygen consumption has an impact on the HTP, again because it consumes fossil-fuel based energy. Since the amount of oxygen required in the Base case is more, it has a higher contribution from this unit than the ATR and CR cases. Next, we look at land use change impacts for the three cases.

The biotic production indicator for occupation (the graph on the left in Figure 10) gives the reduction in biotic production potential of the occupied land for each activity, over the occupation period (per kilogram of gasoline produced). In other words, this is the biomass not produced during that particular activity. \(^{69}\) It can be seen that the ATR and CR cases have a more negative effect than the Base case. The major contributor in the ATR case is the “cultivation and harvesting of timber pine”, while for the CR case it is the ‘energy for harvesting of ley grass’, which essentially involves the use of diesel. Harvesting the fully grown timber results in the land being cleared of biomass, which takes time to regrow to its earlier potential. Thus, overall, during the use of the land, the biotic potential is reduced. Diesel is produced from crude oil, which involves large refinery complexes. These refinery complexes also consume power in large quantities, which is supplied by power plants, which again occupy extensive amounts of land. Thus, all these steps contribute to the negative impact on biotic potential for diesel.

A similar trend can be observed in the occupation phases of the groundwater replenishment indicator (Figure 11, left) and the erosion resistance indicator (Figure 12, left). The groundwater replenishment indicator (occupation), tells us how much groundwater could not be replenished while the land was being occupied, while the erosion resistance indicator defines the capability of the soil to prevent soil loss exceeding the naturally occurring soil erosion. \(^{70}\)

On the other hand, the graph for transformation for the biotic production indicator (Figure 10, right) shows the permanent effects for the three cases, after the land has been transformed irreversibly due to a particular activity. The impacts are measured by the reduction in biotic production of the restored land, compared to the reference situation (when the land was not occupied). Here, all three cases have similar results; the largest effects are seen due to the electricity generation, for which a large amount of land is cleared and also impacts the soil, thus making it difficult to return to its relaxed state. Also, the natural gas in the Base case contributes to the permanent reduction in biotic production, while the timber cultivation and harvesting has an almost equal contribution in the ATR case. Again, a similar trend can be observed for the transformation phase of the groundwater replenishment indicator (Figure 11, right).
However, the transformation impacts on the erosion resistance show a different trend. Here, the Base case has the most negative impact overall, followed by the CR and ATR cases. In all cases, the cooling water results in a higher impact than the other activities, followed closely by the natural gas (only applicable to the Base case). In the previous impact categories the effects of the cooling water are also seen, but in this case, it has the strongest contribution. This could be due to the fact that the cooling water is taken from the ground, which has the potential to affect the soil quality, and thus reduce the resistance of the soil to erosion permanently. Also, natural gas drilling and processing affects the soil in the area in the long term. Conversely, after occupation, the land on which timber pine is cultivated is restored to a state which actually increases the erosion resistance of the soil. However, the overall impacts of the erosion resistance are in the power of E-07 and E-08/year, per kilogram of gasoline; which numerically is not high. Figure 13 shows the impacts of the ATR and CR cases, with reference to the Base case for all CML impact categories; that is, the values for the two new processes have been divided by the Base case value, in order to express the impact compared to the Base case. From the graph, we can see that compared to the Base case, both the ATR and CR have the higher values of TETP, followed by the FAETP and EP. In the POCP category, CR has a higher value than the Base case, while ATR is lower; the high POCP values are due to more waste generated in the CR case. In the GWP and ADP (fossil and elements) categories, the ATR and CR cases are far lower than the Base case, while the impacts in remaining categories are almost the same. The magnitude of the disadvantages for the ATR and
CR cases in some categories exceeds the magnitude of the benefits in the other categories.

3.2.2. Comparison of Primary Energy Demand of the Base Case, ATR and CR. The primary energy demand (PED) or the cumulative energy demand reflects the total amount of energy required for each case. Figure 14 shows that the Base case has a higher demand than the new processes. The PED in the ATR case is 8.39% lower than the Base case, while for the CR case, it is ∼43% lower than the Base case. The major influencer for the Base case is the natural gas feed, and the impacts can be associated with the upstream activities of natural gas. The ATR case also consumes considerable energy for the cultivation and harvesting of timber pine. This could be attributed to the energy put in to cultivate the timber, harvest, and store it, as well as for the saw mill. For the CR case, since the amount of pyrolysis oil required is less, the contribution of cultivation and harvesting of timber pine is lower. However, after the electricity requirement for compressors, the energy for harvesting the ley grass has a significant contribution. Thus, we could say that the Base case is more energy-intensive than both the new processes.

4. CONCLUSION

This work introduces two innovative, inherently energy-efficient processes for the production of gasoline from pyrolysis oil and biogas. The two suggested routes, ATR (autothermal reforming of pyrolysis oil and biogas) and CR (separate, but coupled, steam reforming of pyrolysis oil and catalytic partial oxidation of biogas), are found to have carbon efficiencies of approximately 0.40 and 0.53, respectively.

A life-cycle assessment was conducted to evaluate the environmental performance of the two cases and compare to a Base case, which is production of gasoline from natural gas.
From the earlier graphs showing the contribution of each subunit to the CML impact categories of GWP, AP, and PED, we can see that the activities related to the biomass feed (for biogas and pyrolysis oil production) for the new processes, have an advantage over the natural gas feed. In terms of GWP (which includes land use change effects), the ATR and CR cases are 90% and 47.5% lower than the Base case respectively, while for the PED, they are 8.4% and 43% lower than the Base case, respectively. Moreover, the amount of oxygen consumed in the ATR and CR cases is lower than that in the Base case, which has lower associated impacts in the impact categories. The major contributor to almost all impact categories is the electricity; this is due to the fact that the electricity is sourced from the power grid, which is typically a mix of different kinds of power plants (mostly nuclear and fossil-fuel based plants). These power plants are responsible for a significant amount of emissions, which impacts most of the categories. The use of electricity is also reflected in the subprocesses: oxygen and cultivation and harvesting timber pine, since these units also consume electricity from the grid. The steps related to the harvesting of timber pine and ley grass consume diesel (a fossil-based fuel), which also contributes to the impact categories.

However, in the categories of terrestrial ecotoxicity potential (TETP), photochemical ozone creation potential (POCP), and freshwater aquatic ecotoxicity potential (FAETP), the Base case does better than both new processes. These findings agree with the studies reported in the literature, as stated earlier in the introduction. To reiterate, almost all case studies found that biomass-based fuels and processes presented significant benefits in terms of GHG emissions and energy consumption. However, they find mixed results in the remaining categories, particularly the toxicity, acidification, and eutrophication categories.

Moreover, the impact categories related to land use changes also show that the new cases (CR higher than ATR) have a higher impact in the occupation phases of the biotic production potential and the erosion resistance indicator. The major contributor to this is the cultivation and harvesting of the biomass for the processes. However, in the transformation phases, the CR case has the lowest impact throughout, followed by the Base case and ATR case. Here, impact of the electricity is most visible, followed by that of the cooling water.

In conclusion, both the ATR and CR cases show strong gains in categories such as the GWP, ADP, and PED, and perform slightly better or almost the same as the Base case in the others, with the exception of the TETP, FAETP, and HTP and the land use impact categories. Between the two new routes, ATR has a lower carbon efficiency than CR, but a better environmental profile than CR.

Thus, a clear conclusion cannot be drawn as to whether the new processes are indeed a better choice than the conventional process; this requires one to go a step further by weighting the impact categories based on the requirements of the study, or by carrying out a multicriteria decision-making analysis, and then evaluating the outcome.

5. OUTLOOK

The life-cycle assessment of the ATR and CR cases needs to be subjected to a multicriteria decision-making analysis, in order to be able to state decisively as to whether they are indeed a better option. It is clear that the feedstock affects the environmental footprint of the process considerably, particularly in the land use change categories; and using agricultural, food, or forest waste would reduce the impact associated with cultivation of biomass substantially. A detailed sensitivity analysis of different feed types (and the associated supply chain) will give a better idea of how the type of biomass affects the sustainability of the process. In addition, it would be worthwhile to see whether the transport of raw biomass feedstock affects the overall process. Moreover, the gasoline produced in the process could be used instead of the diesel (for the harvesting step), as well as for the transport of the raw materials. It would be useful to see how this affects the performance of the process. Lastly, a sensitivity analysis could also be carried out by using electricity from different sources, and analyzing how they affect the environmental profile of the processes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.6b04611.

Heat integration by pinch analysis; LCA methodology; calculation for ley grass and timber pine requirement (PDF)

Three snapshots of GaBi plans (Base case, ATR case, and CR case); snapshot of Excel file with LCA results (PDF)

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