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Concentrating-Solar Biomass Gasification Process for a 3rd Generation Biofuel

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A new concept of producing synfuel from biomass using concentrating solar energy as its main energy source is proposed in this paper. The aim of the concept is to obtain an easy to handle fuel with near-zero CO₂ emission and reduced land-use requirements compared to first and second generation biofuels. The concept's key feature is the use of high-temperature heat from a solar concentrating tower to drive the chemical process of converting biomass to a biofuel, obtaining a near-complete utilization of carbon atoms in the biomass. H₂ from water electrolysis with solar power is used for reverse water gas shift to avoid producing CO₂ during the process. In a chemical process simulation, we compare the solar biofuel concept with two other advanced synfuel concepts: second generation biofuel and coal-to-liquid, both using gasification technology and capture and storage of CO₂ generated in the fuel production. The solar-driven third generation biofuel requires only 33% of the biomass input and 38% of total land as the second generation biofuel, while still exhibiting a CO₂-neutral fuel cycle. With CO₂ capture, second generation biofuel would lead to the removal of 50% of the carbon in the biomass from the atmosphere. There is a trade-off between reduced biomass feed costs and the increased capital requirements for the solar-driven process; it is attractive at intermediate biomass and CO₂ prices.

Introduction

Liquid biofuels are seen as one of the few technological solutions currently available to reduce greenhouse gas emissions from transportation (1). Both the European Union and the United States have set near-term targets for having about 5% of their vehicle fuel derived from biomass, and policy makers plan to increase the share. These policies, however, have triggered a string of reports critical of biofuels (2–4). So-called first generation biofuels are essentially based on foodstuff such as sugar, starch, and oil. The crops require substantial inputs of fertilizers, pesticides, and machines, and trigger emissions of nitrous oxide. With the exception of sugar-cane-based ethanol, they offer at best a marginal reduction of greenhouse gas emissions compared to diesel cars when evaluated over the whole life cycle (5–9). However, the greatest disadvantage of first generation biofuels is to compete with food production for scarce agricultural land and water, so that the amount of biofuels that can be

produced from these sources is limited (10). Converting natural ecosystems to cropland produces substantial GHG emissions (6, 11, 12). So-called second generation biofuels are based on lignocellulosic biomass from trees and grasses that can be grown on more marginal land with lower inputs of water, fertilizers, and use of machinery. Lignocelluloses are more complex carbohydrates that require more chemical processing and hence more energy to be turned into a liquid fuel. Second generation biofuels use the energy in the biomass to drive the conversion process, with an energy efficiency of about 50% (13, 14). These fuels hence have larger land-use requirements than some first generation biofuels. Compared to cropland, forest and grassland store significant amounts of carbon in both soil and standing biomass. Analysis has shown that carbon storage in the ecosystem is a crucial factor for the overall climate effect of biofuels (6, 15). A general problem of biofuels, however, is the low efficiency of solar energy conversion by photosynthesis. The highest yields can be obtained from tropical sugar cane and eucalyptus plantations, and they represent efficiencies on the order of 1% (8). For the next generation of biofuel concepts, we hence suggest to produce the energy to drive the conversion process from solar heat instead of biomass. Solar heat can be captured and stored at much higher efficiencies. This means, in essence, to use biomass as a source of carbon to produce convenient, carbonaceous liquid fuels, while obtaining a significant fraction of the energy directly from the sun. Alternatively, nuclear fission or other heat sources could be used to drive the process (16).

In this paper, we present a chemical process simulation of a potential design of a third generation biofuel production facility. The design is based on steam gasification of biomass. The heat for the gasification is provided by a solar concentrating tower. We model the production of methanol, which can be used directly as transport fuel or as input for DME and FT-diesel synthesis. For comparison, we also model the production of methanol using only biomass as a fuel (2nd generation) and using coal as source of both carbon and energy. We assume CO₂ capture and storage of excess carbon produced during the fuel production for both of the alternative scenarios. The land use requirements, resource efficiency, and capital requirements of the systems are evaluated. We do not, however, present a full life-cycle assessment that would also require the assessment of planting, harvesting, and transport, as well as the production of all the industrial and transportation equipment used.

A number of designs of solar-thermal systems for process heat and to produce transport fuels can be found in the literature. They range from proposals for actual systems to experimental investigations of individual processes. Kodama (17) reviews the solarchemical reforming of coal and methane, as well as the dehydrogenative coupling of methane, an endothermic process for the formation of larger hydrocarbons from methane. Fletcher (18) reviews solar-thermal processing, provides a rationale for such an effort, and explains some of the thermodynamics. The focus of the research reviewed is on hydrogen production from water, but other designs including syngas production also receive attention. A more recent review of the solarchemical reforming of methane is provided by Steinfeld (19). Lede provides a review of alternative processes of solarchemical conversion of biomass for chemical synthesis, heat, and electricity production (20). The review covers gasification and pyrolysis approaches which use direct solar radiation. It emphasizes that there is limited experimental research which mostly focuses on biomass gasification processes. The most active research

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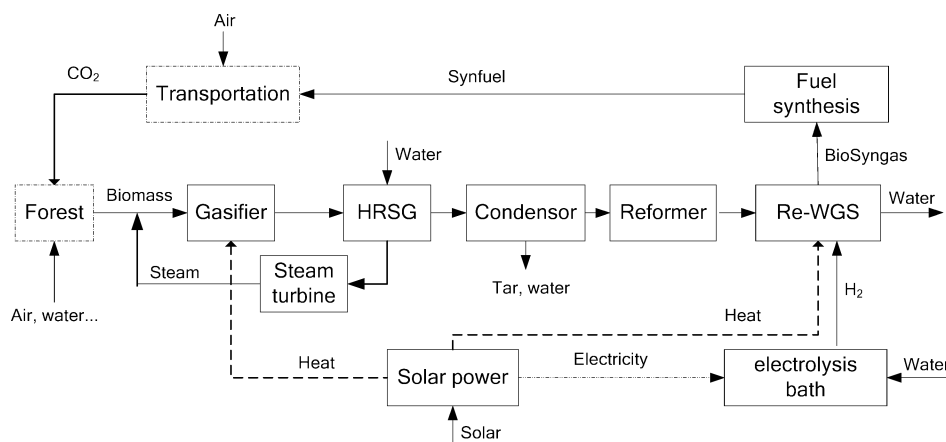


FIGURE 1. Schema of Scenario I: Synfuel synthesis through solar-driven biomass gasification.

seems to address flash pyrolysis (21–23). The modeling work we report here is different in the sense that we do not assume the use of direct solar radiation, but rather assume that this energy is transferred to a standard biomass gasification process, which allows for interim heat storage and hence longer operating hours. Heat transfer and storage, however, is one of the technical challenges in the systems design presented here, and it may in the end be more advantageous to use direct solar radiation as suggested by Lede and colleagues.

Solar power towers generate electricity from sunlight by focusing concentrated solar radiation on a tower-mounted heat exchanger. The system uses hundreds to thousands of sun-tracking mirrors called heliostats to reflect the incident sunlight onto the receiver (24). The dishes of the solar concentrator can achieve temperatures in excess of 1500 °C (25). In a solar power tower, liquid molten salt is pumped from a “cold” storage tank through the receiver where it is heated and then flows on to a “hot” tank for storage. The heat in the “hot” molten salt can be pumped to the other units, such as a steam generating system that produces superheated steam for a conventional Rankine cycle turbine/generator system or the jacket of a chemical reactor to provide the reaction heat, e.g., to a biomass steam gasifier. The molten salt is then returned to the “cold” tank where it is stored and eventually reheated in the exchanger.

Biomass gasification requires more than 700 °C, and for good kinetics 900 °C would be desirable. Different options of heat storage and transfer at higher temperature exist. But for a typical molten-nitrate-salt heat storage and transfer medium system, the reported molten temperature is generally from 290 to 565 °C (24). A liquid metal, such as mercury, could potentially be used up to 2000 °C. Toxicity and reactivity, however, present significant challenges. Recently, Forsberg et al. (26) proposed high-temperature liquid-fluoride-salt systems, which make it possible to increase salt coolant temperature to 700–850 °C or even more. For example, the melting and boiling point of LiF–NaF–KF (46.5–11.5–42) are 454 and 1610 °C, respectively. Based on IEA SolarPACES Implementing Agreement, 2030 technology of solar power tower will exploit a receiver with >1000 °C (24). Thus, with innovation in heat transport technology, high heat capacity and high boiling point molten salt systems may become feasible.

Agrawal et al. (27) have proposed to use solar hydrogen from photovoltaics to provide the energy for converting biomass to a liquid biofuel. Their calculations indicate a reduction of land use required by 60%, so that, as a result, a much larger amount of biofuel can feasibly be produced. The disadvantage with this concept is that the electrolytic production of hydrogen is still very expensive and fairly

inefficient. The use of an intermittent source of electricity such as PV-solar makes it even more expensive to implement such a technology. Solar heat, on the other hand, is more easily produced and can be stored overnight so that a conversion facility can operate around the clock, and with comparatively lower capital cost.

In this work, we provide a process model of solar-driven biofuel production (Scenario I). High temperature heat for gasification is obtained from a molten-salt system in a solar concentrating tower. The H₂ for reverse water gas shift reaction is produced by electrolyzing water driven by solar power. Although a few concepts proposed in Scenario I have not been verified and implemented, the scheme relies on a range of proven technologies in chemical engineering, such as the catalytic design and heat transfer, as well as process design. The traditional conversion of biomass to fuel (Scenario II) and coal to fuel (Scenario III) by gasification were also investigated for comparison. We include CO₂ capture at the process plant in scenarios II and III. The scenarios are based on the current industrial technologies and experimental results in the literature. We evaluate the mass and energy balances of the process facilities. Comparison and analysis for three scenarios are implemented by considering the energy conversion efficiency, resource productivity, land used for biomass growth and for solar energy, and CO₂ emissions, as well as total capital requirement and indicative fuel costs.

Description of Three Synfuel Scenarios

(1) Scenario I: Synfuel Synthesis through Solar-Driven Biomass Gasification. Six main sections are included in the Scenario I: *steam gasifier*, *reverse water gas shift (Re-WGS)*, *hydrocarbon synthesis*, *heat recovery and steam generation (HRST)*, and *solar power system*. The flowsheet of scenario I is shown in Figure 1. Transferring the high temperature heat from the solar concentrator to the gasifier and designing the available configuration of the gasifier are technological challenges. One of the feasible approaches is heating sand (Olivine, also the catalyst of gasification reaction) by hot molten salt from a solar concentrator tower, using a gasifier designed as a fluidized-bed of olivine particles (28). The hot syngas from the gasifier is cooled and cleaned to remove water, particle, tar, and so on, then compressed to the reformer (methane reforming) and then Re-WGS reactor. Additional H₂ from water electrolysis driven by solar power is fed into the shift reactor to convert CO₂ to CO and adjust H₂/CO ratio to satisfy the requirement of the synfuel production. The steam produced by the heat recovery steam generation (HRSG) could be used for gasification. (In Figures 1–3, the block with dash-dotted line means that this block is not simulated in this work, thus the energy and material consumed in the block are not calculated.)

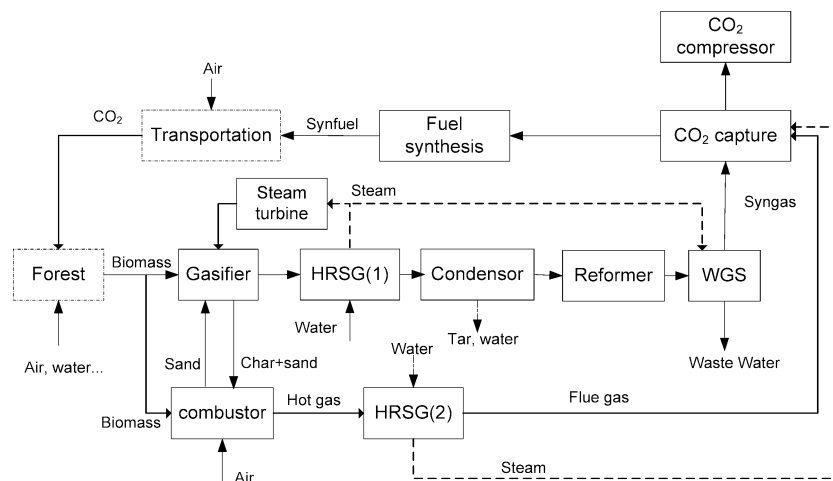


FIGURE 2. Schema of Scenario II: Synfuel synthesis through biomass-fired biomass gasification.

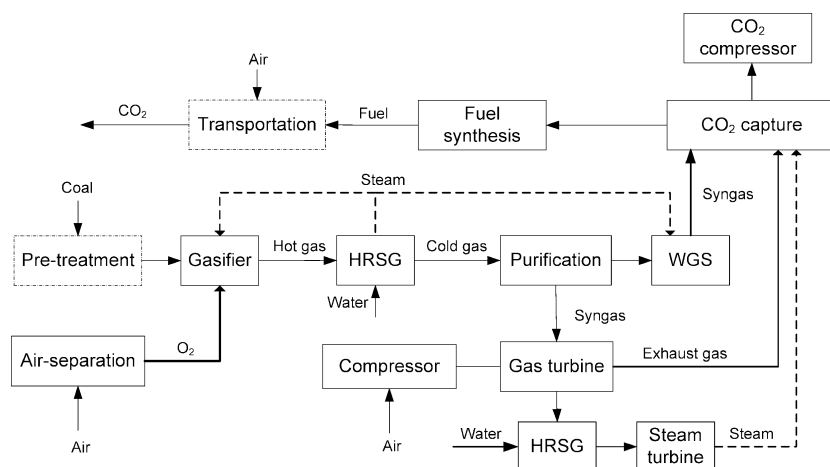


FIGURE 3. Schema of Scenario III: Synfuel synthesis through coal gasification.

(2) Scenario II: Synfuel Synthesis through Biomass-Fired Biomass Gasification with CO₂ Capture. Scenario II is a conventional biofuel process by biomass gasification, but with the potential to add CO₂ capture and compression (Figure 2), reflecting ideas of a carbon-negative energy system (29). Eight main sections are included: *steam gasifier, combustor, reformer, water gas shift (WGS), CO₂ capture and compression, biofuel synthesis, heat recovery and steam generation (HRST), and steam turbine*. The char produced in the gasifier is combusted to provide the gasification heat. In principle, other fuels such as natural gas can be fed into the combustor in case of a shortage of char. In this work, additional biomass serves as the fuel to provide the heat for gasification by combustion. The flowsheet configuration and parameter sets are based on the low-pressure indirect biomass gasification of Battelle Columbus Laboratory (30, 31). The CO₂ in the syngas from the gasifier and the flue gas from the combustor are absorbed using amine-based CO₂ capture technology (32). The steam is produced by recovering heat from syngas and flue gas, as well as the reaction of liquid fuel synthesis. Electricity for pressurizing the syngas before fuel synthesis and compressing CO₂ to 200 bar for CO₂ transport and storage is in part generated by steam turbine shown in Figure 2, in part by a biomass power plant with an efficiency of 43%.

(3) Scenario III: Synfuel Synthesis through Coal Gasification with CO₂ Capture. The flowsheet of synfuel through coal gasification is simulated based on the Shell entrained flow gasifier. Seven sections are included: *gasifier, water gas shift, CO₂ capture and compression, liquid fuel synthesis, heat recovery and steam generation (HRST), and steam turbine*

(Figure 3). The basic flowsheet configuration and data are derived from the literature (33, 34). The gasification reagents are oxygen and steam that is generated from the HRSG in which the hot syngas (1450 °C) heats the boiler water. The pressure in the gasifier is 25 bar. The hot syngas from the gasifier is cooled to 280 °C and depressurized to 9.52 bar before being fed into the water gas shift reactor. The CO₂ in the syngas from the WGS reactor and in the exhaust gas from the gas turbine are absorbed with amine-based method. The total heat and electricity needed by the whole system are from the HRSG, gas turbine, and steam turbine, which means the energy utilization has been integrated in this synfuel production process. The electricity consumption of large-scale cryogenic oxygen plants is approximately 380 KWh/ton O₂ (35).

Methods

The first step was to develop process flow diagrams and to use these along with literature information and research results as well as the practical industry experience to build process simulation models. The mass and energy balance were calculated, and operational parameters were adjusted to optimize feed resource and energy utilization of the whole system. Methods are further detailed in the Supporting Information.

(1) Estimation of the Standard Enthalpy of Formation ΔH_f^0 of a Biomass. The ΔH_f^0 of biomass is important for simulating a biomass gasification process. In this work, we deduced the formula (eq 1) to calculate the ΔH_f^0 of a biomass

TABLE 1. Estimation Results of Three Scenarios with CO₂ Capture and Compression

	Scenario I	Scenario II	Scenario III
technical characteristics			
energy conversion efficiency (%)	60.9	42.0	36.5
fuel productivity (kg fuel/100 kg resource)	121.0	39.9	62.2
land area for biomass growth (m ² /ton fuel/yr) ^a	331	1003	0
land area for solar energy collection (m ² /ton fuel/yr)	51.5	0	0
fuel cycle atmospheric CO ₂ balance (gC/MJfuel)	0	−32	25
cost estimate (2001\$/GJ)			
capital charge	4.0	2.0	2.9
O&M	1.0	0.5	0.7
fuel cost	2.5	8.8	3.8
CO ₂ handling cost	0.0	0.8	0.9
CO ₂ charge (@ \$100/tC)	0.0	−3.2	2.5
total	7.5	8.9	10.8

^a Assuming a yield of 2.5 kg/m²y.

based on the High Heating Value (HHV) correlation developed by Channiwala et al. (35, 36) and combustion reaction of biomass.

$$\Delta H_{f, \text{biomass}}^0 = -\Delta H_{\text{HHV}}^0 + \alpha \Delta H_{f, \text{CO}_2}^0 + \frac{\beta}{2} \Delta H_{f, \text{H}_2\text{O}(l)}^0 + \varepsilon \Delta H_{f, \text{SO}_2}^0 \quad (1)$$

In eq 1, α , β , and ε are the molar content of carbon, hydrogen, and sulfur in the biomass (see Supporting Information). The ΔH_f^0 values of CO₂, H₂O (g), and SO₂ can be obtained from the handbook.

(2) Modeling of Biomass Steam Gasification. Operational parameters of the performance of gasification are reported in ref 28. Prins et al. (35) and Li et al. (37) proposed a “quasi”-equilibrium model to simulate the biomass gasification process. We use experimental data to define the suitable quasi-temperature. We model H₂, H₂O, CO, CO₂, and CH₄ as the only stable gaseous components. We assume no tar formation and a char yield of 30 g/kg biomass (28, 38). Based on iteration, we estimate that a suitable quasi-temperature is about 150–180 °C lower than the practical temperature according to the experimental data from Rapanga et al. (28).

(3) Modeling of Reverse Water Gas Shift Process. In Scenario I, in order to avoid CO₂ product, a reverse water-gas shift (Re-WGS) reaction is designed to react H₂ and CO₂ to form CO and H₂O (39). Re-WGS is an endothermic reaction, and additional heat is required to get a high conversion rate (27). The Re-WGS process was simulated based on the equilibrium model, and the reactor temperature and pressure are assumed as 300 °C and 10 bar.

(4) Simulation of Synfuel Synthesis. Methanol synthesis is an exothermic reaction which is often conducted over a Cu-based catalyst (such as CuO/ZnO/Al₂O₃), at 220–260 °C, 20–40 bar, in a packed bed reactor. To overcome the low one-pass conversion rate of methanol synthesis, part of the unreacted gas is recycled after being separated from the methanol product stream. The methanol reactor is assumed as an isothermal equilibrium reactor based on stoichiometric approach; the Soave–Redlich–Kwong equation is used to describe the thermodynamic properties in this process (40).

(5) Heliostat Land Area Requirement. The Supporting Information documents how the land area required for the heliostats to produce the electricity, hydrogen, and heat used in Scenario I have been calculated.

(6) Land Area Estimation for Biomass Growth. Assuming the biomass (dry) growth rate is φ , then the land needed S_{Biomass} for biomass growth λ (kg biomass /hr) is estimated as eq 2. The treatment and transportation of biomass are not accounted for in the calculation. In general, φ is ranged from 1 to 3 kg/m²/yr (27, 41). We use an optimistic 2.5 kg/m²/yr in this paper.

$$S_{\text{Biomass}} = \lambda \text{ kg/hr} \times 24 \times 365 \div \phi \text{ kg/yr m}^2 = 8760 \lambda / \phi \text{ m}^2 \quad (2)$$

(7) Cost Estimation. Capital costs for the systems were estimated using a combination of capacity factored and equipment-based estimates (30, 42, 43). The capital cost estimates of solar power system were based on ref 24. The detailed lists of factors was taken from ref 30. Fuel data, CO₂ storage cost, and IRR are based on ref 44. For lacking data, rough estimates were produced.

(8) Wood Analysis and Coal Analysis. The ultimate analysis of pellets is 50.7 wt% C, 42.4 wt% O, 6.9 wt% H, and the rest is N. Moisture content is 7.5 wt%, the ash content is 0.39 m%, and the calorific value is 18.86 MJ/kg raw pellets. Bulk density is 688 kg/m³ (45). The composition of the pulverized coal fed into the gasifier in Scenario III is 8.17 wt% O₂, 1.48 wt% N₂, 5.35 wt% H₂, 5.94 wt% H₂O, 75.73 wt% C, 2.98 wt% S, and the others (33). The energy consumptions for pretreating biomass and making coal-water slurry feed-stock were not included in this work.

Results

Simulation results from the three scenario configurations have been analyzed to determine the resource-to-fuel

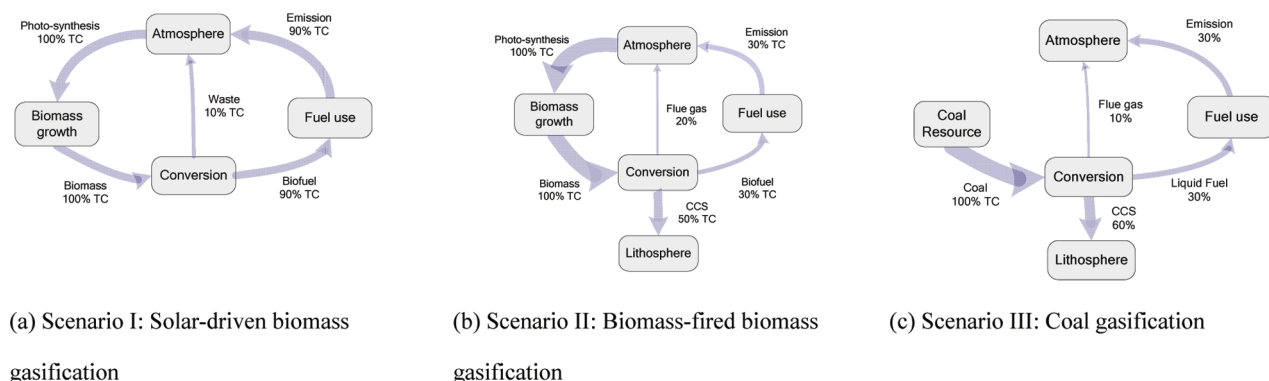


FIGURE 4. Carbon flows of three synfuel synthesis scenarios.

conversion efficiency, land use for biomass growth and solar energy, CO₂ emission and CO₂ fate, carbon-free heat and electricity consumption, and solar Heliostat investment, as well as the total capital requirement for each scenario.

The energy conversion efficiencies in Table 1 are for the process plants (Figures 1–3) and refer to the fuel energy output divided by the fuel, electricity, and steam inputs (eq S3 in the SI). For the calculations of fuel productivity and required land area, the energy input is assumed to be provided by solar energy, biomass CHP, and coal CHP in scenarios I, II, and III, respectively. The fuel cycle atmospheric CO₂ balance indicates that scenario II results in a net removal from the atmosphere of 117 g of CO₂ per MJ fuel produced, while scenario III results in a net addition of 93 g CO₂/MJ to the atmosphere. By comparison, the combustion of gasoline leads to 69.2 g CO₂/MJ.

Figure 4a, b, and c show the carbon flows of three scenarios. In Scenario I, little CO₂ is produced during the process so that CO₂ capture is not needed. Ninety percent of total carbon from biomass is converted to biofuel and emitted to the atmosphere after utilization as transportation fuel. Ten percent of carbon is oxidized and released to the environment. The process is carbon neutral, with the important caveat that emissions due to land use change, harvesting, transport, and production of all required capital is not taken into account in this study.

In Scenario II, 30% of the biomass is used to provide heat for biomass gasification and 20% is used to produce electricity and heat for the process and CO₂ capture and compression. Only 30% of total carbon from the biomass feedstock is converted to fuel. Fifty percent of total carbon is stored in geological formations. The result is a carbon-negative process, removing CO₂ from the atmosphere. In Scenario III, 60% of total carbon from the coal resource is captured and stored geologically, and 30% of total carbon is converted to transport fuel and then released to the atmosphere by utilization.

From the above analysis, we can see that Scenario I will be a good option for resolving two global questions: one is to reduce land use for growing the biomass for energy resource, another one is to avoid potential long-term problems caused by the geological storage of CO₂.

The cost estimates in Table 1 indicate that Scenario I has substantially higher capital costs, but these are more than offset by lower fuel cost. The fuel costs include utility costs (Scenario II) and credits (Scenario III). There is a substantial uncertainty connected to cost estimates in general and for novel technologies in particular, so that cost ranges for the scenarios overlap. There is arguably a large covariance in capital costs among the three designs, but technology risks for solar heat are different from those for CCS plants. The cost estimates for Scenario II are comparable to those in ref 44 but lower than those of Hamelinck and Faij (14). We do not include biomass drying/preparation, assuming in essence a lower fuel price than (14). Higher biomass costs would favor Scenario III > Scenario I > Scenario II. A higher CO₂ price would favor Scenario II > Scenario I > Scenario III. Scenario I is preferred at intermediate CO₂ prices.

Most of the 77 EJ of direct energy use in transportation in 2000 consisted of liquid fuels. Various scenario analyses assume a 2% growth rate, to 114 EJ in 2020. Producing 10% of this energy from second generation biofuels would require 44–130 million hectare (ha), assuming yields of 1–3 kg/m²y. In comparison, cropland today covers 1.5 billion ha. Producing the same amount with third generation biofuels requires 3 million ha for solar power and 22–51 million ha for biomass plantations. Given the concern of the effect of biofuels on land use, food production, and biodiversity impacts (46), reducing the land use by such a substantial amount offers a significant step forward.

Acknowledgments

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Supporting Information Available

Detailed description of the methods and capital costs of three scenarios. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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