Engineering 3 (2017) 166–170

Contents lists available at ScienceDirect

Engineering

journal homepage: www.elsevier.com/locate/eng

Research
Smart Process Manufacturing—Perspective

Artificial versus Natural Reuse of CO_2 for DME Production: Are We Any Closer?

Mariano Martín

Department of Chemical Engineering, University of Salamanca, Salamanca 37008, Spain

ARTICLE INFO

Article history:
Received 22 November 2016
Revised 12 January 2017
Accepted 30 January 2017
Available online 16 March 2017

Keywords:
Solar energy
Photovoltaic
Concentrated solar power
Biomass
Water electrolysis
Dimethyl ether

ABSTRACT

This work uses a mathematical optimization approach to analyze and compare facilities that either capture carbon dioxide (CO_2) artificially or use naturally captured CO_2 in the form of lignocellulosic biomass toward the production of the same product, dimethyl ether (DME). In nature, plants capture CO_2 via photosynthesis in order to grow. The design of the first process discussed here is based on a superstructure optimization approach in order to select technologies that transform lignocellulosic biomass into DME. Biomass is gasified; next, the raw syngas must be purified using reforming, scrubbing, and carbon capture technologies before it can be used to directly produce DME. Alternatively, CO_2 can be captured and used to produce DME via hydrogenation. Hydrogen (H_2) is produced by splitting water using solar energy. Facilities based on both photovoltaic (PV) solar or concentrated solar power (CSP) technologies have been designed; their monthly operation, which is based on solar availability, is determined using a multi-period approach. The current level of technological development gives biomass an advantage as a carbon capture technology, since both water consumption and economic parameters are in its favor. However, due to the area required for growing biomass and the total amount of water consumed (if plant growing is also accounted for), the decision to use biomass is not a straightforward one.

1. Introduction

The rapid increase in carbon dioxide (CO_2) emissions over the last decades is related to the development of industry and transportation. In recent years, there has been a technological effort toward CO_2 capture in order to remove it from the atmosphere. However, the large amount of CO_2 produced annually, which amounts to more than 32 $GtCO_2$ [1], prevents a future in which CO_2 is only sequestered. We need to make use of it. Lately, CO_2 has also been reused as a carbon source. The US Department of Energy presented a diagram of possible uses for captured CO_2 [2]. These include direct use in the food industry (i.e., carbonated beverages); use as an extractant, refrigerant, fire suppressant, or inerting agent; and use for enhanced fuel recovery and for the production of chemicals, polymers, and fuels. CO_2 can be used as a raw material in the production of urea or polycarbonates, as well as in the production of bulk chemicals such as methanol or methane. A number of papers have shown various processes for the transformation of CO_2 into different chemicals via hydrogenation [3]—into methane [4], methanol [5], or dimethyl ether (DME) [6]. In order to transform it into other chemicals, a reduction reaction of the CO_2 is required—the very process that plants perform naturally. Today, biomass-based fuel production uses the CO_2 fixed by plants in the form of hydrocarbons to produce bioethanol, biodiesel, and so forth [7]. Aside from food-linked raw materials, algae and lignocellulosic raw materials such as switchgrass are useful for biomass-based fuel production. As an example, let us focus on diesel substitutes such as DME. DME can be produced directly from biomass-based syngas [8], or obtained using CO_2 and renewable hydrogen (H_2) [6]. For this comparison, it is paramount that the energy source be renewable. In this perspective work, both processes are compared in order to examine the performance of the technologies that reuse CO_2—one being a natural process, and the other

E-mail address: mariano.m3@usal.es

http://dx.doi.org/10.1016/J.ENG.2017.02.002

an engineered process to transform solar energy into power using photovoltaic (PV) panels or concentrated solar power (CSP) facilities.

For a systematic analysis of technologies and of the operation of processes, the mathematical optimization approach is a powerful tool. This analysis involves modeling all the units that form part of the process flowsheet using mass and energy balances, chemical and phase equilibria, experimental data, and rules of thumb. Next, a superstructure of alternatives is built, which includes the major technologies and network flows that allow the processing of a certain raw material or energy source into a product. The model is typically formulated as a mixed-integer nonlinear programming (MINLP) problem. To tackle this problem, numerical routines and/or decomposition algorithms are required [9]. Only after solving the problem can we compare different processes from various sources. Water and energy consumption optimizations are either done simultaneously or performed after the process design. Finally, a detailed economic evaluation is carried out for a more complete comparison of the operating data. The three alternatives are compared in terms of their use of natural resources, including land use and water and energy consumption, and in terms of an economic point of view. It is beyond the scope of this work to develop an integrated metric to compare the alternatives; rather, the aim here is only to describe and compare the results of the analysis and to suggest pros and cons toward the use of different renewable technologies for the production of the same product, DME.

The paper is organized as follows: Section 2 describes the technologies and presents their flowsheets. Section 3 shows the operating information regarding needs and consumptions, and discusses pros and cons of the alternatives. Finally, Section 4 contains some conclusions.

2. Process description and design approach

This section describes three alternative technologies for the production of DME. The first technology consists of the use of lignocellulosic biomass, which can be considered the natural product of CO_2 capture using solar energy. The second and third technologies involve the production of power from solar energy using either PV panels or CSP facilities, and its further use to hydrogenate CO_2 toward DME. The processes are modeled unit by unit, including all heat exchangers, reactors, columns, and so forth, based on first principles, thermodynamic and phase equilibria, rules of thumb, etcetera. A simplified profit is used as an objective function to optimize each process. The selection of the process and operating conditions corresponds to the solution of a mathematical MINLP problem of the following form [9]:

$$\begin{aligned} &\max Z = \text{simplified profit } (x, y) \\ &h(x, y) = 0 \\ &g(x, y) \le 0 \\ &x \in R^n,\ y_i = \{0, 1\} \end{aligned} \tag{1}$$

where the constraints $h(x, y)$ and $g(x, y)$ correspond to the models of the units. The model is solved to optimality in order to determine the operating conditions and the technologies involved in the final flowsheet.

Next, economic evaluations are performed, including investment and production costs. For the investment, the factorial method is used, which allows the estimation of the total investment as a function of the equipment costs. The equipment cost estimation is performed using parametric charts or correlations as a function of a characteristic variable such as a dimension, a mass, or an energy flow. Unit sizing may be needed to compute the equipment's characteristic dimension. It can be carried out by means of short-cut designs of the unit, in order to estimate the heat exchanger area or the column diameter. The production costs include labor, maintenance, raw materials, utilities, administration, and other general expenses [10].

2.1. Biomass-based dimethyl ether

In nature, plants capture CO_2 from the atmosphere and process it via photosynthesis in order to grow. This process takes some months before the biomass can be harvested for further use.

$$CO_2 + 2H_2O + \text{photons} \longrightarrow [CH_2O] + O_2 + H_2O \tag{I}$$

Once biomass such as *Miscanthus* or switchgrass is available, it is processed to obtain syngas and DME. A number of technologies are available to process this biomass into syngas. First, the biomass is gasified. Two technologies are considered. The first technology, direct gasification, uses a single unit that requires feeding with pure oxygen (O_2) in order to avoid gas dilution, and that produces a raw syngas with a high CO_2 content but a low hydrocarbon content. In the second technology, the gasifier and the combustor operate separately, allowing the use of air to burn the char, and producing a raw syngas with a higher hydrocarbon concentration. Next, two reforming modes can be used—partial oxidation or steam reforming—transforming the hydrocarbons into H_2 and carbon monoxide (CO). Although steam reforming generates a larger amount of H_2, it is endothermic. Partial oxidation is exothermic, but the product gas has a lower concentration of H_2. Subsequent gas cleaning for solids and sour gases removal are implemented to purify the syngas. A composition adjustment stage may be needed so that the proper H_2-to-CO ratio is fed to the reactor. DME is produced by following direct synthesis, in a novel one-step technology.

$$CO + 2H_2 \rightleftharpoons CH_3OH \tag{II}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{III}$$

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \tag{IV}$$

The unreacted gas can be either recycled or used within a Brayton cycle for the simultaneous production of DME and power. Fig. 1 provides the superstructure. To determine the optimal set of technologies for gasification, gas reforming, composition adjustment, and operating conditions to process biomass into DME, a mathematical programming approach is used. The structure is modeled using mass and energy balances, chemical and phase equilibria, rules of thumb, and experimental data, such as in the case of the gasifiers. Thus, the problem is formulated as a MINLP problem. The optimal process presented by Peral and Martín [8] involves indirect gasification followed by steam reforming and wet solids removal. DME production is favored over power for current electricity prices.

2.2. Solar-based dimethyl ether

In the artificial scenario, the CO_2 captured by any industry can be reacted with H_2 to produce DME. In order for this process to be renewable, the H_2 must also be renewable. On the one hand, H_2 can be produced from biomass [11]; however, this process does not make much sense, since it returns to the atmosphere the CO_2 that was previously fixed in the form of biomass. Thus, this process only recovers the H_2 from water that was used to build the hydrocarbons. On the other hand, solar energy can be used to split water. In order to compare this process with the biomass-based process, the use of PV panels or CSP facilities is considered to capture solar energy and transform it into power.

Fig. 2 shows the structure of a CSP facility. It consists of the heliostat field, the molten salt circuit, the steam circuit, and the cooling system. Molten salts are heated in a heat exchanger that receives solar energy, and are then stored in a tank. The flow of salts from the tank is regulated over the day. Part of the flow from the tank is