Energy 144 (2018) 279–285

Contents lists available at ScienceDirect

Energy

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

A novel process for CO_2 capture from the flue gases to produce urea and ammonia

Esmaeil Koohestanian, Jafar Sadeghi*, Davod Mohebbi-Kalhori, Farhad Shahraki, Abdolreza Samimi

Department of Chemical Engineering, University of Sistan and Baluchestan, Zahedan, Iran

A R T I C L E I N F O

Article history:
Received 19 July 2017
Received in revised form
6 December 2017
Accepted 7 December 2017

Keywords:
CO_2 capture
CO_2 utilization
Process design
Urea and ammonia synthesis

A B S T R A C T

The paper addresses the production of urea from carbon dioxide and nitrogen in the flue gas of the power plants as an alternative to other proposed and suggested processes. The conventional separation process of CO_2 from flue gases has been so far directed to the methanol synthesis, while nitrogen, as the main part of the combustion product, is ignored. Carelessness about and lack of use of this byproduct is led to the techno-economical failure of the process and cause environmental problems. In this research, to the best of our knowledge, for the first time, the synthesis of urea and ammonia from the combustion of oxy-fuel was investigated and the appropriate and green process was designed and proposed. To enhance economic justification, the process design was carried out using all three main components of the flue gas (CO_2, N_2, and H_2O), along with efficiency increment of the combustion units. Considering of 2036 kg/hr oxy-fuel combustion products, direct removal of 1700 kg/hr CO_2 from the carbon cycle and production of 2856 kg/hr molten urea is estimated, which the latter product worth about 3.5×10^6 US$/year.

1. Introduction

1.1. Background

Separation and purification of carbon dioxide have been common from the past for various reasons and usages such as food industry, metal industry, welding and injection to the oil fields in the process of enhanced oil recovery (EOR). However, in recent years due to the environmental requirements and the effects of greenhouse gases on the climate changes [1], the CO_2 capture and storage (CCS) process have been developed to reduce this pollutant from its main sources such as power stations, petrochemical plants, cement factories, oil refineries, etc. [2,3]. Since most of this pollutant is produced by power stations [4], many studies have been focused on its removal from the power plants flue gases. Generally, three methods of pre-combustion, post-combustion and oxy-fuel combustion have been proposed to separate CO_2 from the flue gases [5,6]. In the method of pre-combustion, fossil fuel is converted to the syngas, consisting of CO and H_2, and after converting CO to CO_2, the hydrogen is separated from the CO_2. In the oxy-fuel combustion, the high purity oxygen obtained from the air separation unit (ASU) is used instead of air in the combustion process. As a result, the concentration of CO_2 in the flue gases is increased, where it can be separated easily after dehydration by the cooling and compression. Furthermore, in the oxy-fuel combustion, due to the elimination of nitrogen, the flame temperature increases and leads to the less fuel consumption. Though higher flame temperatures, specially above 1700 K [7], cause more production of the nitrogen oxides (NOx), as the major pollutant of concern [8], it will not be the main issue in the oxy-fuel combustion because of the low content of nitrogen in the flue gas stream. However, in the oxy-fuel method, in order to control the flame temperature and compensation of removed N_2 from the fuel gas mixture, some of the CO_2 gas is recycled to the combustion chamber [4]. The post-combustion of the CO_2 separation causes minimum changes in the original configuration of the existing power plant [9].

1.2. Carbon dioxide utilization

The separated carbon dioxide can be stored underground in an

---

* Corresponding author.
E-mail addresses: koohestanian@gmail.com, koohestanian@pgs.usb.ac.ir (E. Koohestanian), sadeghi@eng.usb.ac.ir (J. Sadeghi), davoodmk@eng.usb.ac.ir (D. Mohebbi-Kalhori), fshahraki@eng.usb.ac.ir (F. Shahraki), a.samimi@eng.usb.ac.ir (A. Samimi).

https://doi.org/10.1016/j.energy.2017.12.034
0360-5442/

Nomenclature

Abbreviations

ASU	Air separation unit
BFD	Block flow diagram
CCS	Carbon capture and storage
CPU	Compression and purification unit
EOR	Enhanced oil recovery
IEAGHG	International Energy Agency Greenhouse Gas
PFD	Process flow diagram
NOx	Nitrogen oxides
SOx	Sulfur oxides
k_{ij}	Temperature-dependent binary parameters

Equipment

HPC	High pressure condenser
HPS	High pressure stripper
UREA-R	Urea reactor

empty gas reservoirs or used in the EOR process. However, storage of CO_2 in the empty reservoirs is not justified from economical point of view. Furthermore, during natural events such as an earthquake it can be released whereby the CO_2 pollution level can be suddenly raised [10]. Injection of CO_2 into oil fields can decrease the crude oil viscosity and the extraction costs, but does not lead to its removal, while the cost of the sweetening process will be increased, too.

In recent years, the separation of CO_2, not as a waste but as a valuable raw material, and its converting to valuable products, have highly drawn the attention [11,12]. Carbon dioxide is used as a raw material for the production of many petrochemical products specially urea and methanol. To employ CO_2 in each of petrochemical plants, complete assessments of the market demand, other raw materials and the ways that CO_2 can be provided are required [13,14].

Through the following reactions (Sabatier reaction), converting CO_2 into methane and methanol is possible [15]:

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O,\ \Delta H_{298\ K} = -165.0\ \text{kJ/mol} \quad (1)$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O,\ \Delta H_{298\ K} = -49.4\ \text{kJ/mol} \quad (2)$$

According to the thermodynamic point of view and with regard to the range of the required temperature and pressure to perform each of these reactions, converting the carbon dioxide to methane is more probable, as compared to the methanol product [11]. Nevertheless, compared to methane, converting CO_2 into methanol is more favorable due to lower consumption of the expensive hydrogen gas. Also the cheaper storage and the valuable derivatives of methanol such as dimethyl ether, make its production more attractive than methane. If from an environmental point of view conversion of CO_2 into methanol is carefully studied while hydrogen is obtained from the water electrolysis, the production of methanol from CO_2 would be justifiable [16]. In this regard, several units have been so far made that are in operation [17]. The first commercial plant of methanol production from CO_2 using hydrogen from water electrolysis, was constructed in Iceland [17]. However, to prevent the reproduction of CO_2, the electricity needed for the plant operation is better to be provided from the renewable energy sources such as wind and solar energy [12,18]. However, using CO_2 in order to synthesize these products rather than removing it from the cycle, only delays its entrance into the environment.

Another product, obtained from carbon dioxide, is urea. Urea is widely used in the fertilizer industries as a rich source of nitrogen [19]. Urea is non-toxic and has the lowest transportation cost per unit of the nitrogen nutrition. Furthermore, urea is a raw material for the production of many important chemical compounds such as various plastics, resins and adhesives. Some of its derivatives are urea-formaldehyde and urea-melamine-formaldehyde and urea-nitrate explosives material [19]. Reports indicate that, nowadays, approximately 180 Mt/y of urea is produced in the world [20]. To produce this amount of urea, 132 Mt/y of CO_2 is required [20]. The most common method for production of urea is reforming natural gas, producing carbon dioxide and ammonia [21]. Then urea is formed based on the reaction (3) [22]:

$$2NH_3 + CO_2 \leftrightarrow NH_2CONH_2 + H_2O. \quad (3)$$

In fact, the above reaction is composed of two steps. First, the ammonium carbamate (NH_2OCONH_4) is produced from the heterogeneous reaction of ammonia and carbon dioxide as in reaction (4). Then, after the formation of ammonium carbamate in the liquid state, urea is formed by dehydration of ammonium carbamate by reaction (5):

$$2NH_3 + CO_2 \leftrightarrow NH_2OCONH_4, \quad (4)$$

$$NH_2OCONH_4 \leftrightarrow NH_2CONH_2 + H_2O. \quad (5)$$

Carbon dioxide also can be produced from combustion. Considering, CO_2, nitrogen, and water as the main products of the combustion process, capturing of CO_2 and removing water from the combustion gas can lead to produce almost a high purity N_2. The latter product in the reaction with hydrogen provides ammonia by the reaction (6):

$$N_2 + 3H_2 \leftrightarrow 2NH_3,\ \Delta H_{298\ K} = 11.04\ \text{kcal/g-mol}. \quad (6)$$

Therefore, the production of urea by reaction of ammonia with CO_2, which is captured from combustion flue gases, would increase the economic justification of CO_2 capture unit. In addition, the stoichiometry of methanol and urea reactions show that equal hydrogen required in the production of both materials whilst urea has a more demand in the global marketing than all of the obtainable materials from CO_2 [23]. Moreover, it is remarkable that more than half of the CO_2 produced in the world is used for urea production [24]. Thanks to its global demand that is approximately three times higher than methanol, the global price of the urea is higher than methanol [20]. Regarding to this fact, its production would be more feasible, specifically when the process design is carried out according to the combustion gas contents. As in addition to CO_2 removal, nitrogen, the largest byproduct of the combustion process, can also be used.

1.3. The urea synthesis

Generally, three main industrial methods exist for the urea production from the natural gas feedstock as shown in Fig. 1. As it is shown in all of these methods, after purification and desulfurization, the natural gas converts to the syngas in a reforming unit. Due to the serious poisonous nature of CO_2 molecules to the ammonia production catalyst, this component should be removed and reduced to less than 1% in other units such as CO_2 separation, methanation and/or cryogenic units. Furthermore, this leads to decrease the size of equipment, operating and total costs, and increases the conversion rate in the ammonia unit. Finally, CO_2 and