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Review Article

BrOx cycle: A novel process for CO_2-free energy production from natural gas

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ABSTRACT

Currently, the combustion of fossil fuels is the major anthropogenic source of CO_2 and the main reason for the significant increase in its atmospheric concentration over the past decades. Despite the increase in fossil fuel consumption in recent years, the available reserves have actually increased, indicating that the use of fossil fuels is limited less by their availability than by the emissions of CO_2 associated with their combustion.

Energy can be generated from methane without concomitant CO_2 emissions by means of a bromination-oxidation (BrOx) cycle. This process comprises two exothermic reaction steps, namely methane bromination and hydrogen bromide oxidation, with a bromine recycle from the latter to the former, that result in an overall exothermic reaction in which methane and oxygen yield water and solid carbon, thus avoiding CO_2 production.

Thermodynamic and kinetic simulations have been performed that show the feasibility of the BrOx cycle. The influence of temperature, residence time and feed composition on methane bromination reaction was studied and indicates that carbon formation starts at temperatures as low as 500 °C for excess methane, while temperatures over 750 °C are necessary in order to achieve noticeable carbon formation when working with excess bromine. The composition of the carbon produced has been determined and the mass fraction of bromine-containing by-products has been found to decrease with increasing reaction temperatures.

Contents

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Introduction

Energy consumption and the standard of living are closely correlated and thus humanity needs abundant and uninterrupted energy supplies. Over the 20th century, global energy consumption has steadily increased, reaching more than 500 EJ in year 2014 [1]. This trend is expected to continue in the coming decades due to the predicted growth in both the worldwide population and economy.

In 2014, fossil fuels represented more than 80% of the total primary energy demand of the OECD (Organisation for Economic Co-operation and Development) members [1]. This energy is primarily obtained via the combustion of coal oil and natural gas, which implies the formation of CO_2, a by-product that is routinely released into the atmosphere. As a consequence, its atmospheric concentration has steadily increased over the past decades [2], which scientific consensus considers to be the main cause of climate change [2]. Recently, at the 2015 United Nations Climate Change Conference (COP21) held in Paris, an agreement was achieved, that intends to limit the increase in the global average temperature to less than 2 °C above pre-industrial levels [3]. In order to do so, a dramatic reduction of CO_2 emissions is inescapable. Since the largest anthropogenic source of CO_2 is that derived from energy generation, avoiding or minimising the associated emissions is the most direct strategy.

One approach for reducing energy-derived CO_2 emissions is to expand the use of renewable energy. A good example of this is the energy transition (*Energiewende*) that has been adopted in Germany, which aims to reduce greenhouse gases emissions by 40% by 2020 and by 80–95% by 2050 [4]. Although the share of renewable energy in Germany's gross power supply has reached 32.5% in 2015 [5], the impact on global energy production is negligible. Additionally, several studies predict that fossil fuels will remain the predominant energy source for the next decades, still supplying at least 75% of the world energy demand in 2040 [6].

Despite the increased fossil fuel consumption over the last century and contrary to popular belief, the proven reserves of fossil fuels have not decreased in the past few decades, but actually increased as exemplified by natural gas, whose proven reserves were 117.6 Tm^3 in 1992 and 187,8 Tm^3at the end of 2011 [1]. In addition, if natural gas from unconventional sources, such as shale gas, coal-bed methane or methane hydrates, is taken into account, the estimates of the gas supply available can be measured in centuries [7]. Naturally, not all unconventional resources are technically or economically exploitable at the present time, but this situation may soon change as new extraction technologies are developed. The shale gas boom provides a good example of such a development in the past. Although well-known, shale gas has remained non-exploitable for decades until a combination of new technologies, namely hydraulic fracturing (fracking) together with horizontal drilling and, most importantly, high gas prices made its economic exploitation feasible [8].

The aforementioned demonstrates that the use of fossil fuels is less restricted by their availability than by the CO_2 emissions resulting from their combustion. In view of this and from the fact that replacing the existing infrastructure for extraction, processing, transportation and storage would be extremely expensive, and in the short term, unfeasible, the decarbonisation of energy production from fossil fuels is a promising strategy to counter climate change.

CCS (Carbon Capture and Storage) has been proposed to decarbonise fossil fuels by capturing the CO_2 before or after combustion and sequestering it either under the ocean or subcutaneously. It is a controversial technology that lacks the acceptance of a large section of the public and entails many uncertainties regarding costs, long-term reliability and storage capacity [9]. Moreover, up to 40% of the energy being generated may be sacrificed by this process.

Another approach that enables CO_2-free energy production from fossil fuels is methane pyrolysis. Despite the endothermic methane pyrolysis, the hydrogen produced can react exothermically with oxygen thus leading to a net reaction in which roughly half the total energy available is released, with solid carbon and water as the only by-products. This process has been widely studied, but it still is not technically feasible, mainly due to heat exchange issues and the fact that it is only kinetically feasible at temperatures above 1200 °C [10,11].

The BrOx cycle is a novel process that enables the use of natural gas for energy production without accompanying CO_2 emissions. It comprises two exothermic reactions, which result in the same net reaction as the combination of methane pyrolysis and hydrogen combustion. The BrOx cycle has thus the advantage of avoiding any heat transfer to an endothermic reaction at high temperatures.

In the BrOx cycle, methane and bromine are first fed to a reactor, where they react to yield solid carbon and hydrogen bromide (Eq. (1)). An excess of bromine is used to ensure that methane is completely consumed. Following subsequent separation of the solid carbon, that can be carried out with a combination of a cyclone and a filter to remove the fine particles, the remaining gaseous product stream is fed to a second reactor, in which hydrogen bromide reacts with an