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Direct decarbonization of methane by thermal plasma for the production of hydrogen and high value-added carbon black

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ARTICLE INFO

Article history:

Received 3 March 2017

Received in revised form

29 August 2017

Accepted 3 September 2017

Available online xxx

Keywords:

CFD

Nucleation

Growth

Population balance model

ABSTRACT

In the prospect of a large scale deployment of Renewable Energy for electricity production, plasmas will definitively be a major option to get tuneable, high temperature enthalpy sources without direct CO₂ emissions. This paper focuses on the direct decomposition of methane for the simultaneous synthesis of hydrogen and high value-added carbon black.

After a review of gas phase carbon particle nucleation and growth physico-chemical phenomena, a new original model for the plasma decomposition of methane is presented. The model solves a reactive turbulent flow in a 3D geometry. The nucleation is based on a detailed reaction mechanism and the particle growth is handled by a sectional method. This model opens the way towards a better understanding of carbon particles gas phase nucleation and growth and consequently to a fine control of high value-added carbon black grades.

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Introduction

In the current worldwide energy context characterized by climate change and fossil fuel depletion, the massive use of renewable energy appears essential for the future. The large scale deployment of renewables faces major limitations, among which:

1. the resource variation and its predictability,
2. the supply-demand matching,
3. storing the electricity produced from the renewables in electro-chemical form (i.e. batteries) can be challenging,

especially for mobile applications where high energy densities are required,

4. high initial investment costs (CAPEX), even though major cost reductions have been achieved in the past few years, particularly in the PV and wind turbines areas.

In this prospect, energy storage issues will probably be decisive. Green synthetic fuel, including H₂, are expected to become a major primary energy storage player [1,2], provided the fact that the conversion of electricity into green synthetic fuel can be done efficiently and cost effectively [3–6].

The conversion of low carbon content electricity into green synthetic fuel is particularly suitable if it can be achieved

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<https://doi.org/10.1016/j.ijhydene.2017.09.021>

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together with a partial (or total) fuel decarbonization. In this perspective, three main options are especially interesting:

1. the use of biomass as raw material,
2. the CO₂ retro-conversion,
3. the direct decarbonization of fossil fuels.

While, the first two options have been extensively studied all over the world, the direct decarbonization pathway has been seldom explored [7–14].

Thermal plasmas offer many benefits for the conversion of electrical to chemical energy, providing a flexible, controllable and tunable heating source without direct CO₂ emissions [15]. In addition, they are particularly suitable for endothermic processes and when high temperatures are required; such conditions being often encountered in most thermochemical processes, especially for combustion-based processes.

First efforts related to the decomposition of hydrocarbons in a plasma were published in 1920 by Rose [16]. The method involved a vessel with two electrodes for the pyrolysis of a gaseous feedstock flow. From 1920 to 1990 many carbon black companies followed Rose's footsteps, among which are Goodyear [17], Ashland Oil and Refining [18], Continental Carbon [19], Phillips Petroleum [20,21]. In his paper, Gonzalez et al. [22] provides a comprehensive survey of studies carried out in the field.

In the 90's, the Norwegian engineering company KVAERNER (now AKKER-KVAERNER), in collaboration with SINTEF-NTNU Prof. BAKKEN's group in Trondheim-Norway [23], has been intensively operating on the setup of a DC plasma system dedicated to the co-production of carbon black and hydrogen from natural gas and several patents were issued by Lynum S. et al. [24–30]. The plasma torch technology was based on the generation of a high velocity blown arc plasma rotating at the tip of two concentric cylindrical hollow graphite electrodes under the combined effect of a strong axial gas flow associated with an external magnetic coil. In 1992, a first 3 MW plasma pilot was successfully installed and tested in Sweden at ScanArc HOFORS facilities [30]. In 1997, KVAERNER started the construction of a first industrial plant in Karbomont (Canada) with a 20,000 tons carbon black and 70 Million Nm³ hydrogen capacity. Unfortunately, the development of the process was stopped in 2003 due to technological issues in the carbon black quality control.

Almost concurrently, Fulcheri and Schwob started in 1993, the development of a 3-phase Alternative Current plasma prototype [31]. This technology led to four patents [32–35] and number of papers [23,36–46]. A comprehensive review of the main three phase AC plasma torch achievements is given in Ref. [47].

Other works based on inductively coupled plasma and arc technologies were led in Canada by Soucy's group [48], Meunier et al. [49–52], in the US by Fincke et al. [53], in Korea by Kim et al. [54,55], Cho et al. [56] and in China by Zhang et al. [57], Sun et al. [58]. Finally, in the 2010's, the company ATLANTIC HYDROGEN, located in New Brunswick (Canada), developed the CarbonSaver™ concept based on a

non-thermal plasma technology. This concept was centered on the partial decarbonization of grid gas to produce natural gas enriched with hydrogen and re-introduce it into the grid. Carbon black being a byproduct of the process. The concept was developed up to the pilot scale, but this development stopped in 2016 when the company was assigned into bankruptcy [59–61].

Co-production of carbon black and H₂

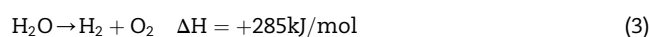
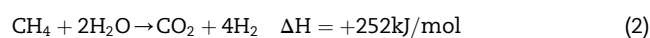
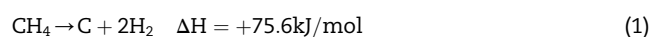
Hydrogen is the ultimate form of decarbonized fuel. 98% of the hydrogen production comes from fossil fuels reforming (mostly by methane Steam Reforming) [62,63] with huge direct impacts on CO₂ emissions corresponding (world average, source DOE 2013) to 12 kg CO₂ eq. per kg of H₂. Giving rise to 720 Million tons CO₂ eq. emissions per year representing by itself no less than 2.25% of the total worldwide CO₂ emissions.

Since the industrial revolution, carbon black production steadily increased to reach current a production of 12 million tons per year [64]. Last news on the Worldwide Carbon Black Market says the demand will continue to grow and it is expected a production of 20 million tons by the year 2020. 90% of the production being used in the tire industry and 95% being produced with the furnace process [65]. This process relies on the incomplete combustion of different heavy carbonaceous feedstocks. It is also characterized by direct CO₂ emissions with an average amount around 4 kg CO₂ eq. per kg of carbon black, giving rise to more than fifty million tons carbon dioxide emissions annually and accounting around 0.125% of the Total Worldwide Emissions [66].

The principle of the new plasma process aims to replace these two existing processes, both characterized by high environmental impacts, by a single environmental friendly process allowing the simultaneous synthesis of pure hydrogen and solid carbon directly splitting natural gas thanks to an outer electric energy source.

The major objectives are the replacement of two combustion methods thanks to the use of a flexible external energy supply and the co-synthesis of two valuable chemicals without direct CO₂ emissions with 100% carbon yields [67].

Regarding thermodynamic figures, let's notice that the standard enthalpy reaction of methane dissociation related to hydrogen production (Eq. (1)) is thermodynamically less costly than steam reforming (Eq. (2)) with 37.8 kJ versus 63 kJ per H₂ mole respectively. It is also worth noticing when comparing plasma cracking of methane with water splitting (Eq. (3)), that the production of H₂ by direct methane cracking is thermodynamically 8 times less costly than the production of H₂ from liquid water splitting with 37.8 kJ/(H₂)mol against 285 kJ/(H₂)mol respectively.



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