Fuel 117 (2014) 870–875

Contents lists available at ScienceDirect

Fuel

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

Co-gasification of petroleum coke and biomass

Vera Nemanova *, Araz Abedini, Truls Liliedahl, Klas Engvall

Department of Chemical Engineering and Technology, Chemical Technology, KTH Royal University of Technology, 100 44 Stockholm, Sweden

HIGHLIGHTS

- Co-gasification of biomass and petroleum coke in an atmospheric bubbling fluidised bed and thermogravimetric analyzer.
- Synergetic effect between biomass and petroleum coke was observed.
- The activation energy for pure petcoke is 121.5 kJ/mol, for the 50/50 blend it is 96.3, and for the 20/80 blend – 83.5 kJ/mol.
- Biomass ash has a catalytic effect on the reactivity of petcoke due to the alkali and alkaline earth metals present in ash.

ARTICLE INFO

Article history:
Received 4 July 2013
Received in revised form 5 September 2013
Accepted 17 September 2013
Available online 12 October 2013

Keywords:
Activation energy
Biomass
Co-gasification
Fluidised bed
Petroleum coke

ABSTRACT

Gasification may be an attractive alternative for converting heavy oil residue – petroleum coke into valuable synthetic gas. Due to the low reactivity of petroleum coke, it is maybe preferable to convert it in combination with other fuels such as biomass. Co-gasification of petroleum coke and biomass was studied in an atmospheric bubbling fluidised bed reactor and a thermogravimetric analyser (TGA) at KTH Royal University of Technology. Biomass ash in the blends was found to have a catalytic effect on the reactivity of petroleum coke during co-gasification. Furthermore, this synergetic effect between biomass and petcoke was observed in the kinetics data. The activation energy E_a determined from the Arrhenius law for pure petcoke steam gasification in the TGA was 121.5 kJ/mol, whereas for the 50/50 mixture it was 96.3, and for the 20/80 blend – 83.5 kJ/mol.

1. Introduction

Currently, the world production of petroleum coke is steadily expanding due to an increased consumption of oil and oil-related products [1–3]. The low price, high calorific value, low ash content and abundant availability of petcoke make it a very attractive fuel.

Petroleum coke (petcoke) is a by-product produced from heavy crude oil residues by thermal cracking processes – delayed or fluid coking (Fig. 1). Bayram et al. [4] reported that from 1 tonne of crude oil approximately 31 kg of petcoke is produced. Petroleum coke is a black solid material consisting of polycyclic aromatic hydrocarbons with low hydrogen content. The typical elemental composition of petcoke depends on the crude oil origin, but usually it is composed of C: 91–99.5%, H: 0.035–4%, S: 0.5–8%, (N + O): 1.3–3.8% and the rest is metals [5].

The manufacture of carbon anodes for the aluminium smelting industry, graphite electrodes for steel production and also nonferrous industries are the main non-energy applications of petcoke [5]. In Russia petcoke usage is higher than supply due to the demand in aluminium and electrode industries. In 2005 more than 650 thousand tonnes of petroleum coke were imported from China (65%), Turkmenistan, Japan, Kazakhstan, England and the United States [6].

According to Akpabio and Obot [7] around 75% of the world's petroleum coke is used in the energy sector (mostly in North America). In the past, petroleum coke has often been burned as fuel in boilers for heat and power production. However, the current increasing use of natural gas, which is more convenient and cleaner to burn, has decreased the demand for petcoke [8]. Therefore, new alternatives for utilisation of petroleum coke are of interest. Gasification may be an effective option for converting petcoke into syngas [9].

Gasification is a thermo-chemical process in which feedstock undergoes partial oxidation reaction with an oxidising medium (oxygen, air, carbon dioxide or steam) to produce permanent gases. The process consists of several steps: drying, pyrolysis, gasification and combustion, occurring simultaneously inside a gasifier. The product composition, including solid, liquid and gas phases, depends on feedstock (type of fuel, moisture, composition) and gasification operating conditions (oxidising medium, gasifier type, temperature, pressure etc.) [10].

* Corresponding author. Tel.: +46 768447559.
E-mail address: nemanova@kth.se (V. Nemanova).

0016-2361/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.fuel.2013.09.050

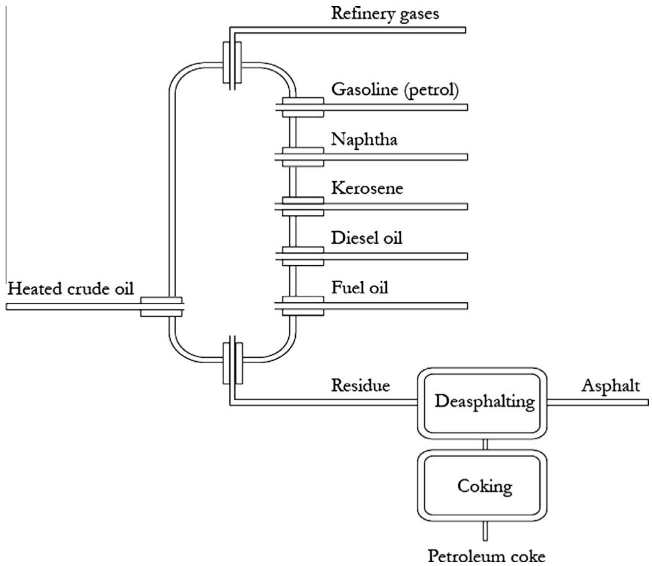

Fig. 1. Schematic view of petroleum coke production from crude oil.

Due to the high fixed carbon content in petroleum coke, it may be complicated to gasify separately [11,12]; therefore it is, perhaps, preferable to convert petcoke in combination with additional fuels such as coal or biomass.

Fermoso et al. [13–15] investigated gasification of a mixture of coal, petcoke and biomass at atmospheric and high pressure in a fixed bed reactor. The results showed that binary (coal–biomass) and ternary blends (coal–petcoke–biomass) have some synergetic effects that enhance gas production.

Zhan et al. [12] used a thermogravimetric system, TherMax 500, to gasify Chinese petroleum coke and lignite with carbon dioxide. They reported low reactivity of petcoke, due to its small BET surface area and carbon network structure similar to graphitic carbon. However, when petcoke was mixed with lignite the reactivity increased.

There are also other studies where petcoke is gasified using different catalysts to increase its low reactivity. Zhou et al. [16] tested the catalytic activity of iron species for CO_2 petcoke gasification. They found that the gasification reactivity of petroleum coke was enhanced with higher gasification temperature and increasing iron species concentration.

Several researchers have carried through simulations and modelling in regard to petcoke conversion into permanent gases [17–19], and others have investigated co-gasification of petcoke and coal [1,11,20] and the ternary mixture (petcoke–coal–biomass) [13–15]. However, there are no studies on co-gasification of petcoke and biomass. The aim of the present work is to investigate the effect of biomass on the reactivity of petroleum coke by co-gasifying in a bubbling fluidised bed reactor. Several tests with different petcoke contents mixed with biomass have been carried out in the gasifier. The reactivities of petcoke, biomass and various petcoke–biomass blends were also determined by thermogravimetric analysis.

2. Materials and methods

2.1. Materials

Pine pellets in the size range of 1.5–2 mm and ground and sieved petroleum coke (1–1.5 mm) provided by Statoil, Norway were used in the experiments. The results of ultimate and proximate analysis are listed in Table 1.

Table 1
Ultimate and proximate analysis of pine pellets and petroleum coke.

	Pine pellets	Petroleum coke
Proximate analysis, as delivered		
Moisture, wt%	4.5	0.5
Ash, wt%	0.5	1.4
Volatiles, wt%	76.5	6.0
Fixed carbon (by diff.), wt%	18.5	92.1
Lower heating value (MJ/kg)	19.2	36.2
Ultimate analysis, dry basis		
Carbon, wt%	47.7	92.3
Hydrogen, wt%	6.3	3.4
Nitrogen, wt%	0.16	0.95
Oxygen (by diff.), wt%	45.3	0.7
Sulphur, wt%	<0.012	1.168

At first glance petroleum coke seems to have better properties compared to biomass, such as higher heating value and higher carbon content. However, petcoke also contains significantly more sulphur. Pinto et al. [21] have examined the influence of different catalytic materials on removal of sulphur and halogens compounds during co-gasification of coals with different types of wastes, such as pine, petcoke and polyethylene. They reported that the presence of dolomite in the bubbling fluidised bed led to the highest sulphur reduction. However, this paper focuses on the gasification process and does not touch upon sulphur contamination or the consequences thereof.

2.2. Gasification setup

Two series of experiments have been carried out: gasification tests performed in 5 kW bubbling bed and thermogravimetric analyses of different mixtures of petroleum coke and biomass in the thermogravimetric analyser (TGA).

The atmospheric fluidised bed gasification system includes a fuel feeder, a gas supply system, gas preheater, and a bubbling fluidised bed gasifier. A schematic view of the gasifier is shown in Fig. 2.

The gasification reactor consists of a fluidised bed (an inner diameter of 0.05 m and a height of 0.30 m) and a freeboard (a

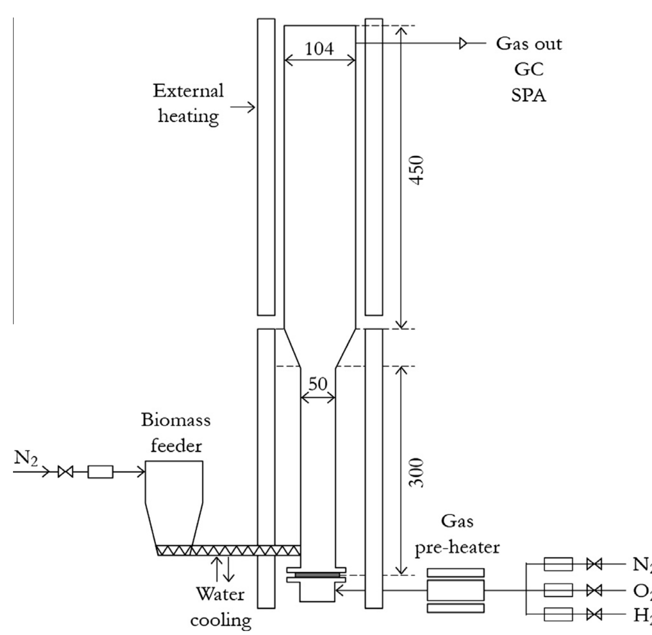

Fig. 2. Schematic view of the KTH atmospheric fluidised bed reactor.