Fuel 197 (2017) 209–216

Contents lists available at ScienceDirect

Fuel

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

Review article

Transformation and roles of inherent mineral matter in direct coal liquefaction: A mini-review

Wen Li [a,*], Zong-Qing Bai [a,*], Jin Bai [a], Xiao Li [b,*]

[a] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China
[b] School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221008, PR China

HIGHLIGHTS

- Transformation and roles of inherent mineral matter in DCL are briefly overviewed.
- Pretreatment methods of low-rank coals to enhance the oil yields are proposed.
- Challenges in investigating transformation and roles of inherent mineral matter in DCL.

ARTICLE INFO

Article history:
Received 10 November 2016
Received in revised form 10 February 2017
Accepted 13 February 2017
Available online 23 February 2017

Keywords:
Direct coal liquefaction
Mineral matter
Product distribution
Roles and transformation

ABSTRACT

Since direct coal liquefaction (DCL) was invented, it has been a promising technology for the efficient utilization of coal resources and the mitigation of the oil crisis. Generally, coals are regarded as mixtures composed of organic matter and mineral matter. The mineral matter content and nature of coal is highly variable and has been proved to significantly influence the thermal behavior of coals in DCL. Therefore, a clear and comprehensive understanding of the transformation and roles of inherent mineral matter in DCL process is really necessary for guiding the oil yield enhancement and moderating the reaction conditions. After direct liquefaction, the mineral matter would be enriched in the residues. Investigations on transformation and roles of inherent mineral matter can be beneficial for the efficient utilization of the residues as well. In view of the great importance of mineral matter to DCL, this paper briefly summarizes the research progress on the transformation and roles of inherent mineral matter in DCL process, and especially focuses on the major mineral matter in coals. As suitable feedstocks for DCL, the low-rank coals are typically rich in exchangeable metallic species (a kind of mineral matter) which can reduce the oil yield in DCL, hence a detailed discussion of transformation and roles of exchangeable metallic species in DCL is given here and two pretreatment methods of low-rank coals to enhance their oil yields are also proposed.

Contents

* Corresponding authors.
E-mail addresses: liwen@sxicc.ac.cn (W. Li), baizq@sxicc.ac.cn (Z.-Q. Bai), cumt_lixiao@163.com (X. Li).

http://dx.doi.org/10.1016/j.fuel.2017.02.024
0016-2361/

1. Introduction

1.1. Overview of DCL process and the behaviors of mineral matter in liquefaction

Direct coal liquefaction, which is known as DCL, refers to the process that involves direct hydrogenation of coals at relatively high temperatures and pressures [1,2]. It can be also viewed as a reductive pyrolysis process in which raw coal is directly converted to liquid products by reacting with hydrogen in hydrogen-rich solvents [3]. Since it was invented by Friedrich Bergius and patented in 1913, the investigations on DCL have attracted much interest worldwide [4–6], especially in recent years [7–9]. Even though many challenges and difficulties, such as the unclear reaction mechanism and kinetics, need to be got over [10], the DCL is still of great strategic importance to relieve the demand for oil. In countries which are short of oil resources and primarily rely on coals, especially in China, the concern over sustainable development of energy sources has further motivated investigations into DCL due to their own declining coal reserves [11–13].

Basically, coals are composed of organic matter and mineral matter [14,15]. The former part mainly consists of polycyclic aromatics, hydro-aromatic, and heterocyclic clusters joined by linkages. The mineral matter in coals originates from inorganic elements that are associated with the organic matter, pore water, and detrital minerals [3]. As an intrinsic part in coals, the mineral matter has been recognized to be active components in DCL and could catalyze transformation of the organic matter [16,17]. For instance, the mineral matter is considered to act as an internal diluent which could minimize agglomeration of coal particles and lead to more effective diffusion of hydrogen to the sites of bond rupture [18]. Similarly, a remarkable reduction on the total conversion and oil yield in liquefaction was observed due to removal of some mineral matter by coal beneficiation (the concentration of inorganic matter) [7]. The conversion of coal to liquid products has also been found to increase as the mineral matter content and the concentration of iron and titanium in the coal increased [19]. However, on the other hand, the mineral matter may also have detrimental effects on direct liquefaction, such as poisoning of catalysts and ash-related issues. Moreover, the mineral matter can possibly play a negative role in the donor extraction and result in undesirable dehydrogenation of the solvent [20], which is definitely adverse to the oil yields.

1.2. Scopes and aims of this review

In view of the complicated and dual roles of mineral matter in DCL, a clear and comprehensive understanding of transformation and roles of inherent mineral matter in DCL can not only potentially provide references for enhancing oil yield but also to moderate reaction conditions. Furthermore, the mineral matter would be enriched in the residue (DCLR) after liquefaction [21]. The investigations on transformation and roles of inherent mineral matter are beneficial for efficient utilization of the residue as well. Therefore, this mini-review briefly overviews the scientific research progress on transformation and roles of inherent mineral matter in DCL, and especially focuses on the major mineral matter in coals. Since the low-rank coals (suitable feedstocks for direct liquefaction) are typically rich in exchangeable metallic species, much attention has been paid to them. It has been shown that the exchangeable metallic species in low-rank coals are detrimental to the oil yield in direct liquefaction and the demineralization treatment of low-rank coals can increase the oil yield in DCL due to removal of the exchangeable metallic species. However, the demineralization treatment of coals, such as hydrochloric acid treatment, will inevitably bring about some problems in practice, which includes the expense of the treatment, corrosion to the equipment, and treatment of sewage. Therefore, in order to enhance the oil yield and make DCL more comparable to other technologies, two feasible pretreatment methods of low-rank coals, including solvent swelling and thermal treatment, are also proposed in this review for the better performance of low-rank coals in DCL.

2. Inherent mineral matter in coals

Organic matter and mineral matter co-exist in coal structure. Nevertheless, compared with the organic matter, the mineral matter has less values in the efficient utilization of coals. From the coal structure point of view, they can be viewed as a diluent, which take place of useful organic matter with inert components that are easily turned into ashes after being burnt [22]. Besides, the mineral matter can also bring about severe and undesirable slagging, fouling, and corrosion problems associated with the coal handling [23–26].

The occurrence modes of mineral matter differ from each other in many ways. According to the classification method proposed by Ward [22], the mineral matter in coals can be broadly divided into three types, namely:

(1) Discrete mineral matter (crystalline or non-crystalline);
(2) Exchangeable metallic species that associated with the organic structure of the coal matrix;
(3) Inorganic substances that dissolved in the pore water of coal.

In high-rank coals, the discrete mineral matter are typically the most abundant species [27] and mainly composed of silicates, carbonates, sulfides, and, sulfates [17] with different chemical structures and molecular sizes. In contrast, for the low-rank coals, exchangeable metallic species dominate and are commonly present in the form of carboxylate [28]. The reason why the concentration of the metallic species decreases with increasing of coal rank is that the exchangeable metallic species are structurally associated with the oxygen-containing functional groups and these functional groups are typically more abundant in low-rank coals. The exchangeable mineral matter can be easily washed away by some chemical reagents [29], such as ammonium acetate solution and