



# Direct liquefaction of lower-rank coals and biocoals with magnetically separable catalysts as a sustainable route to fuels



Martin Trautmann, Swen Lang, Yvonne Traa\*

*Institute of Chemical Technology, University of Stuttgart, Stuttgart, Germany*

## HIGHLIGHTS

- For the first time: magnetically recoverable catalysts for sulfur-free and sulfur-containing coals.
- The higher the metal dispersion, the better the liquefaction activity of the DCL catalysts for low-rank coals.
- Environmental sustainability: improved biocoal liquefaction.

## ARTICLE INFO

### Article history:

Received 2 October 2014

Received in revised form 15 December 2014

Accepted 6 January 2015

Available online 3 February 2015

### Keywords:

Direct coal liquefaction

Heterogeneous catalysis

Magnetic separation

Nanosized fumed oxides

Hydrothermal carbonization

Biocoal

## ABSTRACT

Direct coal liquefaction (DCL) encompasses the catalytic conversion of coal by hydrogen and high temperatures in presence of a solvent and can be used to produce transportation fuels on a commercial scale. DCL economy suffers from its severe reaction conditions (up to 20 MPa hydrogen pressure and reaction temperatures up to 728 K). Industrial catalysts are of low activity since only cheap disposable iron-based catalysts are used. We tested two groups of highly active low-rank coals, one “bitumen-rich” brown coal with a high aliphatic content and a biocoal from the hydrothermal carbonization (HTC) of biomass employing novel catalysts. The oil yield (up to 71 wt.%) and the oil quality from the direct brown coal liquefaction with a small catalyst amount of nanostructured Co/SiO<sub>2</sub> or Co/SiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> showed promising results for further upscaling. The liquefaction of the biocoal with low amounts of Ni/TiO<sub>2</sub> (oil yields up to 42 wt.%) proved to be a meaningful perspective especially for environmental concerns. Furthermore, Co/SiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> and Ni/TiO<sub>2</sub> could be recovered and recycled by magnetic gradient, with only small decreases in their catalytic activity.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

Direct coal liquefaction (DCL), invented by Friedrich Bergius in 1913 [1], encompasses the catalytic conversion of coal by hydrogen and high temperatures in presence of a solvent and was used to produce transportation fuels on a commercial scale in the first half of the past century especially in Germany and Great Britain [2–4]. As the economically more attractive crude oil processing became the method of choice, DCL vanished almost completely from the industry [2–5]. The only exception is the Shenhua DCL process (17 MPa, 728 K) with a 1 Mt y<sup>-1</sup> production plant for liquid fuels in Inner Mongolia, China [3,6]. Several other attempts to reestablish the DCL technology failed since the oil price could stabilize at a low level [5]. DCL economy suffered from its severe reaction

conditions (up to 70 MPa hydrogen pressure and reaction temperatures up to 763 K) [2–5,7]. Nevertheless, after World War II there have been many successful efforts, especially for building DCL pilot plants, in order to decrease the hydrogen pressure below 20 MPa during the operation mode [2–4]. The process economics are always estimated by the relation between the barrel price of a crude oil equivalent out of DCL and the current crude oil price per barrel [8,9]. Most of the documented and investigated processes refer to high-rank coals (bituminous or subbituminous coals) [2–5,7]. Industrial catalysts are of low activity since only cheap disposable iron-based catalysts were used in order to keep the operating costs low [2–5,7]. The main problem of low-rank coals as an alternative is the high oxygen content [3] which causes the consumption of expensive hydrogen yielding water. Therefore, a proper catalyst development is necessary in order to produce high value hydrocarbons which can balance this effect economically. The mentioned Shenhua DCL uses high volatile bituminous coals [10,11]. The combination of a low-rank coal, which has a higher reactivity than high-rank coals [7], and an efficient catalyst

\* Corresponding author at: Institute of Chemical Technology, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany. Tel.: +49 711 685 64061; fax: +49 711 685 64065.

E-mail address: [yvonne.traa@itc.uni-stuttgart.de](mailto:yvonne.traa@itc.uni-stuttgart.de) (Y. Traa).

could help to decrease the severity of the process conditions and therefore the capital costs, which are the major cost component for direct coal liquefaction [7–9,12].

Usually, low-rank coals have H/C molar ratios around 0.9 [2,3] and an organic structure as it is proposed by Hüttinger and Michenfelder [13]. Since higher-ranked coals consist of more polyaromatic rings, like it is proposed by Shinn [14], they are more difficult to liquefy and require severe DCL conditions [2–5,7]. Since aliphatic C–O and C–C bonds, which are more abundant in low-rank coals, have lower bond dissociation energies than aromatic bonds, which are more abundant in high-rank coals [13,15,16], the reactivity of low-rank coals is higher [7]. Schobert points out the excellent potential of lignites for DCL [17]. Many processes for North American lignites were investigated in the past, e.g., the Solvent Refined Coal II process and the Wilsonville liquefaction plant yielding 60 and 50 wt.% oils each, by using iron-based catalysts [17]. Jackson and Larkins reported comprehensively about the direct liquefaction of Victorian brown coal and come to the conclusion that efficient process conditions comprise pressures up to 20–30 MPa and temperatures of at least 723 K with a sulfided iron catalyst [18]. However those conditions are economically not efficient. We claim that the development of a better catalyst is necessary to unleash the whole potential of brown coals or lignites. Additionally, the structure of the low-rank coal should be considered. Therefore a brown coal with a high aliphatic content could be beneficial for lowering the reaction conditions, and this has been shown before [19]. Such “bitumen-rich” brown coals can be obtained by selective mining technologies, e.g., from brown coal seams in Central Germany [20], possess H/C molar ratios up to 1.25 and have already been shown to be promising for DCL reactions in our previous works [19,21].

By introducing a novel nanostructured Co/SiO<sub>2</sub> DCL catalyst, we were able to obtain oil yields up to 55 wt.% out of the premium coal and to do one catalyst recycle without a significant loss in activity [19,21]. Besides Wang et al. [22] and Shadle et al. [23], there are hardly any publications about the DCL of bitumen-rich coals. Since we used a cobalt catalyst, the state of the art for comparable results regarding the catalyst recovery procedure, the catalyst type (cobalt) or similar oil yields is shown. The two-stage Shenhua DCL process yields 65 wt.% oils in fuel grade with coal dissolution in the first stage and liquid upgrading in the second, but uses a disposable iron gel catalyst (GelCat) in the first stage [3,24]. GelCat is a complex Fe–S compound which is formed out of pyrite and ammonia [3,24]. The only industrial process that took advantage of catalyst recovery is the former H-Coal process, whereby Ni–Mo/Al<sub>2</sub>O<sub>3</sub> and Co–Mo/Al<sub>2</sub>O<sub>3</sub> were used in a single-stage coal conversion [3,25]. The catalyst particles could be partially removed by gravity separation with consecutive recycling, nevertheless the oil yield was only 33 wt.% [3,25]. In literature, there are two interesting approaches for the direct liquefaction of brown coals using cobalt catalysts. The first is by Sugano et al., whereby the cobalt was introduced by ion exchange of Co with coal carboxyl groups [26]. This procedure was successful for obtaining good oil yields (58 wt.%) but the catalyst could not be recovered [26]. Secondly, Song et al. used soluble Mo–Co–S complexes which were impregnated onto the brown coal in order to have a high catalyst dispersion yielding 50 wt.% of oil [27]. Those results match with the claim of Derbyshire that catalysts having high dispersions, namely a high contact area between the macromolecular coal molecule and the active catalyst sites, show high DCL activities [12]. Derbyshire also points out the importance of sulfur as a promoter in DCL [12].

In the first part of this paper, we deal with the need of a more active DCL catalyst by increasing the metal dispersion of our Co/SiO<sub>2</sub> catalysts used in previous studies [19,21], by an improved thermal treatment. In addition, we employ a novel magnetic SiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> support for a better catalyst recovery. In combination

with the DCL of a reactive low-rank premium (bitumen-rich) brown coal, these measures improve oil yields and, qualitatively speaking, the overall process economy.

The second part of this paper is mainly connected to environmental concerns which are not considered within the DCL of conventional coals at all. Not only the pollution control costs for companies [28], but also the damage caused by emissions (especially CO<sub>2</sub>) from the European Pollutant Release and Transfer Register industrial facilities in 2009 estimated to at least 102–169 billion Euro [29], reveal the pressing need for alternative routes in the development of future technologies.

One solution could be the production of so-called “second-generation biofuels” via DCL. Second-generation biofuels are mainly produced out of biowaste [30]. The DCL of biocoals which are produced by the hydrothermal carbonization (HTC) of biomass was proposed by Bergius at the beginning of the last century and has not been considered for several decades [31]. In our previous publication, we could show that the DCL of biocoals, from a wide range of biomass raw materials, is under modern liquefaction conditions superior to other biomass liquefaction techniques in literature [32]. The combustion gases of the thus produced biofuels could be recycled for plant growth, and the plants could be again energetically densified by HTC and the following DCL to biofuels [32]. This alternative route could be economically and ecologically beneficial, since no new CO<sub>2</sub> emissions are generated [32]. However, this technique is still in its infancy and has to be further investigated. Therefore, some criteria for “bio-petroleum” established by Wang et al. have to be fulfilled first [33]. The values for a bio-petroleum comprise an H/C molar ratio >1.5, a higher heating value ( $HHV_{oil}$ ) > 40 MJ kg<sup>-1</sup> and an oxygen content  $w_O$  < 6.0 wt.% [33]. Our biocoal DCL yielded up to 32 wt.% biooils which could fulfill the last two criteria using a Ni/TiO<sub>2</sub> catalyst at pressures of 21 MPa and temperatures of 673 K [32].

In order to achieve better results under milder reaction conditions, we lowered the temperature to 623 K and increased the metal dispersion of the nickel catalyst, which is recoverable since our biocoal does not include organic sulfur [34] which normally destroys the magnetic recoverability of Ni/TiO<sub>2</sub> due to sulfidation [19,21].

## 2. Experimental

### 2.1. Materials

The premium “bitumen-rich” brown coal “HOME1” and the normal brown coal “HOME3” were kindly provided by MIBRAG. A sample of the “Biocoal” was obtained from SunCoal and produced out of plant remains. The pretreatment and storage methods of the coals are described elsewhere [19,32]. The results for the higher heating values, the proximate and the ultimate analysis for the three coals are shown in Table 1. Acetic acid (100%), sulfur (purity > 99%) and tetralin (purity ≥ 98%) were purchased from Merck. Nickel(II)nitrate hexahydrate (purity ≥ 98%), *n*-pentane (purity ≥ 98%) and pyridine (purity ≥ 99%) were obtained from Sigma-Aldrich. Cobalt(II)nitrate (purity ≥ 97.7%) was purchased from Alfa Aesar, toluene (purity ≥ 99%) from Honeywell. Hydrogen (5.0), nitrogen (5.0) were obtained from Westfalen. Aeroxide TiO<sub>2</sub> P90 (fumed titania, purity ≥ 99%), Aerosil 300 (fumed silica, purity > 98%) and MagSilica BS<sup>®</sup> (designated as SiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>) were kindly provided by Evonik.

### 2.2. DCL procedure

For all direct coal liquefaction reactions, a Parr MiniBench Top Reactor 4570 (250 cm<sup>3</sup>) was used. Biocoal or brown coal (10.0 g

Download English Version:

<https://daneshyari.com/en/article/205618>

Download Persian Version:

<https://daneshyari.com/article/205618>

[Daneshyari.com](https://daneshyari.com)