



# Effect of calcium additive on product yields in hydrogasification of nickel-loaded Chinese sub-bituminous coal



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## HIGHLIGHTS

- Ni–Ca catalyst reduces the reaction temperature and hydrogen pressure.
- Reactivity order: 1 wt% Ca > 0.5 wt% Ca > 1.5 wt% Ca > 2.0 wt% Ca > 0 wt% Ca.
- Ca makes Ni disperse on coal well, retards Ni sintering and poisoning.
- Ni–Ca catalyst causes the tar molecules to be hydrogenated before hydrocracking.

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## ABSTRACT

Hydrogasification of Chinese sub-bituminous coal was performed in a fixed-bed reactor to study the effects of Ni and Ni + Ca dual catalysts on the yields of light hydrocarbon liquids (HCL) and gaseous products (GPs). In the presence of calcium, a high yield of HCL and GPs was obtained. The main components in tar were light aromatic hydrocarbons (LAHs) such as BTX and naphthalene. The product yields strongly depended on the amount of co-loaded calcium. The maximum yields of LAHs and GPs were achieved to be 2.15 wt% (0.85 wt% of BTX and 0.7 wt% of naphthalene) and 51.51 wt% (CH<sub>4</sub>, CO, CO<sub>2</sub> and C<sub>2</sub>–C<sub>3</sub>), respectively, when using 5% Ni + 1% Ca dual catalysts at 750 °C and 1.0 MPa. The addition of Ca promoted the conversion of oxygen-containing species and aromatics to H<sub>2</sub>O, CO, CO<sub>2</sub>, CH<sub>4</sub> and BTX.

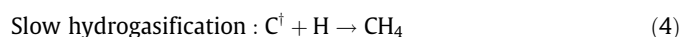
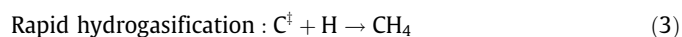
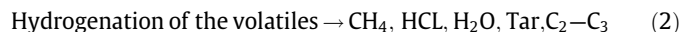
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## 1. Introduction

Coal deposits in China are abundant compared with crude oil and natural gas. In the 21st century, coal will continue to play an important role as one of the main energy sources. Typical industrial utilization of coal include combustion of pulverized coal, gasification, fuel gas production and carbonization. In recent years, the capacity of producing natural gas is limited and cannot satisfy the huge demand, which stimulates more interest in producing substituted natural gas (SNG) through coal hydrogasification.

Coal hydrogasification, the direct gasification of coal with pure hydrogen for production of SNG and/or light hydrocarbon liquids (HCL) consisting of BTX (benzene, toluene and xylenes) and PCXN (phenol, cresol, xylenols and naphthalene), was extensively studied in the 1970s and 1980s. Mechanism of the coal hydrogasification proposed by Jüntgen [28] shows that coal pyrolysis produces

radicals (–CH<sub>3</sub>, –CH<sub>2</sub> from the C–C bridges, O from other bridges and larger ring systems containing some free radicals) by cracking the bridge carbons that have the lowest bonding energies and dissociating the aromatic ring units. CH<sub>4</sub>, HCL, Tar, H<sub>2</sub>O and C<sub>2</sub>–C<sub>3</sub> hydrocarbons are generated by the recombination of radicals and their reaction with hydrogen, CO<sub>x</sub> is produced by cracking of the carboxyl groups and phenolic groups. The main pathways of hydrogasification including consecutive and parallel are given below: (C and H are used as symbols and not in the strict meaning of stoichiometry).



where C<sub>v</sub>, C<sup>‡</sup>, C<sup>†</sup> represent the carbon of volatiles, reactive carbon and inert carbon, respectively. Currently, a lot of research has been

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performed on coal hydrogasification under a high hydrogen pressure and temperature [1–13]. The yields of gas and light hydrocarbon depended on coal type and reaction conditions [2]. The HCL products reached maximum value at 800–850 °C [4,5]. Maximum CH<sub>4</sub> yield was obtained at hydrogen pressure of 7 MPa [7]. However, direct coal hydrogasification has several difficulties such as the need for high temperature and hydrogen pressure, low reaction rate, strong thermochemical suppression at high temperatures, low carbon conversion, and unattractive economy [6].

Catalytic hydrogasification is more beneficial as the reaction could occur under mild conditions (lower temperatures and H<sub>2</sub> pressure), and the carbon conversion as well as the reaction rate could be effectively improved. Nickel metal has been proved to be a very active hydrogasification catalyst. Interestingly, Haga et al. [14,15] reported on the enhancement of catalyst activity by adding alkaline earth compounds and aluminum nitrate to nickel metal. Reaction at lower temperatures (400–700 °C) was promoted by adding Mg, Ca, Ba, and Al salts. Reaction at higher temperatures (above 750 °C) was, however, promoted only by Ca salt. The effect of Ca salt on hydrogasification of carbon, catalyzed by nickel, was studied as a function of pressure up to 3.0 MPa, using pitch coke (C:98%) and activated carbon (C:92%) as the main substrate [16]. Elevated pressures of hydrogen resulted in very high conversions of the carbon. The effect of calcium additive in hydrogasification of nickel-loaded coal char was studied at 750–900 °C and H<sub>2</sub> pressure of 0.1–3.0 MPa [17]. The promoting effect increased with an increase in the amount of added Ca. The hydrogasification of Yallourn char [18] and its catalysis by nickel metal was studied at 0.1 MPa. Nickel showed catalytic activity at loading levels as low as 0.1 wt%. Suzuki et al. [19] focused on hydrogasification of demineralized birch char co-loaded with 3.4 wt% Ni and 0.7 wt% Ca to examine the catalytic effect of the binary system. Total conversion reached 100% when temperature was above 700 °C.

The aforementioned studies on mixed catalyst systems were carried out mostly utilizing model carbon materials or simple wood chars and coal chars, they are more simpler than raw coals. Raw coal is a complex heterogeneous material with various chemical and physical properties, and catalysis in coal hydrogasification is significantly affected by the properties of coal. Therefore, it is meaningful to verify whether or not the Ni + Ca catalyst system works effectively for coals. Ohtsuka et al. [20] investigated the hydrogasification of brown coal in the presence of nickel metal at 600 °C and found that carbon conversion reached 80% with loaded nickel. Murakami et al. [21] studied the hydrogasification behavior of Loy Yang brown coal with ion-exchanged nickel species. The peak of methane evolution appeared at 587–737 °C. They [22] also studied the pyrolysis behavior of nickel–calcium-loaded Loy Yang brown coals and indicated that calcium additive delayed the agglomeration of nickel species.

Nevertheless, the effect of calcium additive on hydrogasification of nickel-loaded sub-bituminous coal has been rarely reported on product distribution including the yields of oils, water and HCL. In this paper, we reported the effect of calcium on hydrogasification behavior of nickel-loaded Chinese sub-bituminous coal. The effect of calcium loading on coal hydrogasification is evaluated with respect to the product distribution, gas evolution profile, light aromatic hydrocarbon liquid and the coal char to further understand the hydrogasification process of nickel–calcium-loaded coal.

## 2. Experimental activity

### 2.1. Materials

A Chinese sub-bituminous coal (Wangjiata coal) was used in this work. The coal was crushed and sieved to 75–150 μm after being dried in vacuo at 105 °C for 2 h. Table 1 shows the proximate

and ultimate analyses of the coal. The catalyst precursor, nitrate of nickel, was impregnated into coal from aqueous solution in the presence or absence of calcium nitrate and mixed 45 min by ultrasound. After impregnation, excessive water was removed in a water-bath at (40–60 °C) and the impregnated coal sample was dry under vacuum (100–105 °C). The sample loaded with nickel alone and that with both nickel and calcium was denoted as ‘Ni’ and ‘Ni + Ca’, respectively. The amounts of the catalytic component and the Ca salt are expressed as the nominal weight percentage of each metallic element relative to coal, irrespective of the working state of the material.

### 2.2. Experimental setup

The experimental apparatus of the coal hydrogasification system are shown in Fig. 1. The main components of the pressurized fixed-bed systems were: coal feed hopper, fixed-bed reactor, pressure control, accumulative flow meter, electric furnace, temperature control, K-type thermocouple, deep cooling trap, ice trap, gas bag, and gas meter. A sieve plate at the bottom of the reactor supported the bed material and provided a uniform distribution of gas. The flow rates of N<sub>2</sub> (99.99%) and H<sub>2</sub> (99.99%) were controlled with an accumulative flow meter. The reactor tube made from stainless steel pipe (40 mm i.d and 1200 mm length) was heated electrically. The temperature was measured with a K-type thermocouple immersed in the fixed-bed reactor tube. The connecting pipe between the reactor and the cold trap was maintained at approximately 400 °C to prevent tar from condensation. Two tar traps connected in series were cooled with ethane-diol/ice: the ethane-diol was cooled to –22 °C and circulated to the cold trap by a circulating pump; the ice trap was filled with n-hexane to collect the hydrocarbon liquid product. The non-condensable gas was collected with a gas bag for analysis.

### 2.3. Production and collection of products

Hydrogasification of coal was carried out at temperature of 750 °C [14]; and pressure of 1.0 MPa [16] under the following conditions: the coal sample was placed in a static bed (800 mm in length) and heated from ambient temperature to 750 °C at the rate of 100 °C/min. A hydrogen flow rate of 4.4 L (STP)/min was used to eliminate the effect of mass transfer. At the beginning of each test, the coal sample was placed in the feed hopper with nitrogen flowing through the system at 3.0 L/min for 20 min to guarantee an inert atmosphere. After 30 min, the reactor was heated with the electric furnace to the desired temperature, which was controlled by a K-type thermocouple, and the heating time is about 90 min. After the temperature reaching the desired temperature, N<sub>2</sub> was switched to H<sub>2</sub> with flow rate of 4.4 L/min, then the coal sample was charged into the reactor immediately. After this, the oil product was collected with ethane-diol/ice traps and the tar adhering to the surfaces of the stainless steel tubes was dissolved with tetrahydrofuran (THF). Non-condensable gas was continuously collected with a gas bag every 15 min. The experiment lasted for 60 min long. After which, char was collected from the reactor and weighted. The n-hexane in the ice trap and THF were drained

**Table 1**  
Properties of the Wangjiata coal.

Proximate analysis (wt%, d)			Ultimate analysis (wt%, daf)				
VM	A	FC	C	H	N	S	O <sup>a</sup>
31.41	22.11	46.48	69.59	4.35	0.78	0.60	24.68

VM: volatile matter; A: ash; FC: fixed carbon; d: dried basis.

<sup>a</sup> By difference.

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