



## Full Length Article

## A Preliminary investigation of CO effects on lignite liquefaction process

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## ABSTRACT

This paper made a preliminary investigation of CO effects on lignite liquefaction process. The Schütze method coupled with an elemental analyzer was adopted for directly determining the O contents of liquid and solid materials, and the O balance, variation amounts of water, and CO consumptions were calculated quantitatively for liquefaction processes. It was found that the two reactions which were the water-gas shift reaction and the reaction between CO and organic structures of coals, occurred distinctly in the liquefaction process with CO atmospheres, and were simultaneously strengthened by the catalysts. The simultaneous occurrence of the two reactions played the roles of reducing the water production, elevating the coal conversion, and promoting the asphaltene (AS) and preasphaltene (PA) production.

## 1. Introduction

Lignite is regarded as an abundant and inexpensive resource accounting for 13% of the coal deposits in China [1]. It is a kind of preferred coals for direct liquefaction, due to its high reactivity [2–5]. However, its high oxygen and moisture contents limit its utilization in direct liquefaction, due to a large hydrogen consumption for removing O and a large energy consumption for drying [6–9]. In view of this, some researchers used syngas (or CO) and H<sub>2</sub>O as a hydrogen source for lignite liquefaction [10–16]. Fischer et al. [10] pointed out that the use of CO and H<sub>2</sub>O could liquefy lignite easily. Hata et al. [11] found that the coal conversion, which was basically equivalent to that in pure hydrogen, increased to 90.1% under syngas and H<sub>2</sub>O as hydrogen source. Shui et al. [12], Subagyono et al. [13], and Guo et al. [14,15] drew a similar conclusion that the coal liquefaction activity under the system of syngas (or CO) and H<sub>2</sub>O (or complex solvent of H<sub>2</sub>O and organic solvent) appeared higher than that under the traditional system of H<sub>2</sub> and organic solvent. Our investigation [16] showed that the conversion and oil yield from Shengli lignite liquefaction under the system of syngas and complex solvent were obviously higher than those under the system of H<sub>2</sub> and organic solvent (especially higher production of PA). Summarily, the utilization of syngas (or CO) and H<sub>2</sub>O as a hydrogen source is quite advantageous for lignite liquefaction. Therefore, in order to the further development and application of the lignite liquefaction technology using syngas (or CO) and H<sub>2</sub>O as a hydrogen source, it is very imperative to

make some investigations on the liquefaction process with syngas (or CO) and H<sub>2</sub>O, especially the following issues. What are the effects (or roles) of CO and H<sub>2</sub>O on the liquefaction process? How do the effects (or roles) of CO and H<sub>2</sub>O occur in the liquefaction process?

This paper is only focused on the investigation of the CO effects (or roles) on the liquefaction process. From a plenty of investigations on the topic [17–24], it could be found that CO assuredly took some roles on the liquefaction process, and the roles of CO could be generally summarized as follows: a production of hydrogen from the water-gas shift reaction of CO and H<sub>2</sub>O to provide hydrogen source for liquefaction reaction, and a more activity of produced hydrogen to stabilize free radicals in liquefaction process. Obviously, these roles of CO have been accepted universally by many researchers and scholars [18,21,25–27]. Besides the above roles, the following issues are not still known or understood. If CO takes some other effects (or roles) on liquefaction process or not? If so, what are the effects? Presently, the relevant investigations (or reports) on this topic are very scarce, and only a literature [28] mentioned that CO had a probable role for directly removing O. The special investigations on this topic were not found. For this, this paper made a preliminary investigation on the lignite liquefaction process (such as the water variation after liquefaction, the distribution of liquefaction products, the O contents of liquid and solid products, and the CO consumption for liquefaction reaction, etc.) with CO atmospheres, aiming at obtaining a further understanding of the CO effects on liquefaction process.

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**Nomenclature**

CSARB	coal sample on as received basis
THN	tetralin
THF	tetrahydrofuran
TN	toluene
HEX	<i>n</i> -hexane
GP	gaseous product
HS	HEX-soluble fractions
W	water
HSWT	integrant for HS, THN, and W
HSW	HSWT excluding THN
AS	HEX-insoluble but TN-soluble fractions
PA	TN-insoluble but THF-soluble fractions
CT	catalysts
RSM	integrant of RS, ashes of CSARB, and CT
RS	RSM excluding ashes of CSARB and added CT (if any)
BR	reaction atmosphere before liquefaction reaction
Y	yield, %
m	mass, g
V	volume of gaseous phase in the liquefaction reactor, L
P	pressure of liquefaction reactor at 25 °C, MPa
G	concentration of <i>j</i> gas components in GP, %
M	molar mass of <i>j</i> gas components in GP, g/mol

T	water content, %
Q	variation amount of water, g/10 g CSARB
C	O contents, %
N	O mole number, mmol/10 g CSARB
TN <sub>B</sub>	total mole number of O element in reactants, mmol/10 g CSARB
TN <sub>A</sub>	total mole number of O element in products, mmol/10 g CSARB
R	ratio of TN <sub>B</sub> and TN <sub>A</sub>
E	total consumption amounts of CO mmol/10 g CSARB
E <sub>1</sub>	consumption amount of CO from water-gas shift reaction, mmol/10 g CSARB
E <sub>2</sub>	consumption amount of CO from the reaction of CO and coals, mmol/10 g CSARB
Z	gas mole number of <i>j</i> gas components, mmol/10 g CSARB
D	generation amount of <i>j</i> gas from the water-gas shift reaction, mmol/10 g CSARB

**Subscripts**

<i>i</i>	product (AS or PA)
<i>j</i>	gas components (CO, CO <sub>2</sub> , H <sub>2</sub> , or C <sub>1</sub> -C <sub>4</sub> )
<i>k</i>	matters (CSARB, HWST, AS, PA, or RSM)

**2. Experimental****2.1. Materials**

The used raw coal was a kind of lignite from Xilinhaote Coal Mine of Inner Mongolia Autonomous Region in China. The raw coal was ground to below 0.2 mm, subsequently dried at 100 °C for 12 h, and stored hermetically as coal sample on as received basis (termed as CSARB) for liquefaction experiments. The CSARB was made a proximate analysis

according to the National Standard of China (GB/T 212-2008), and the contents of its moistures ( $M_{ar}$ ), ashes ( $A_{ar}$ ), volatile matters ( $V_{ar}$ ), and fixed carbons ( $FC_{ar}$ ) are 3.52%, 10.94%, 38.05%, and 47.49%, respectively. The C, H, N, S, and O contents of the CSARB, which were determined by the elemental analyzer (introduced in Section 2.3), are 61.52%, 4.13%, 1.04%, 0.40%, and 25.68%, respectively. The tetralin (THN) and Fe<sub>3</sub>O<sub>4</sub> were used as solvents and catalysts for liquefaction experiments, respectively. N<sub>2</sub> (99.999%) and CO (99.999%) with high purity were used in liquefaction experiments. All used solvents and

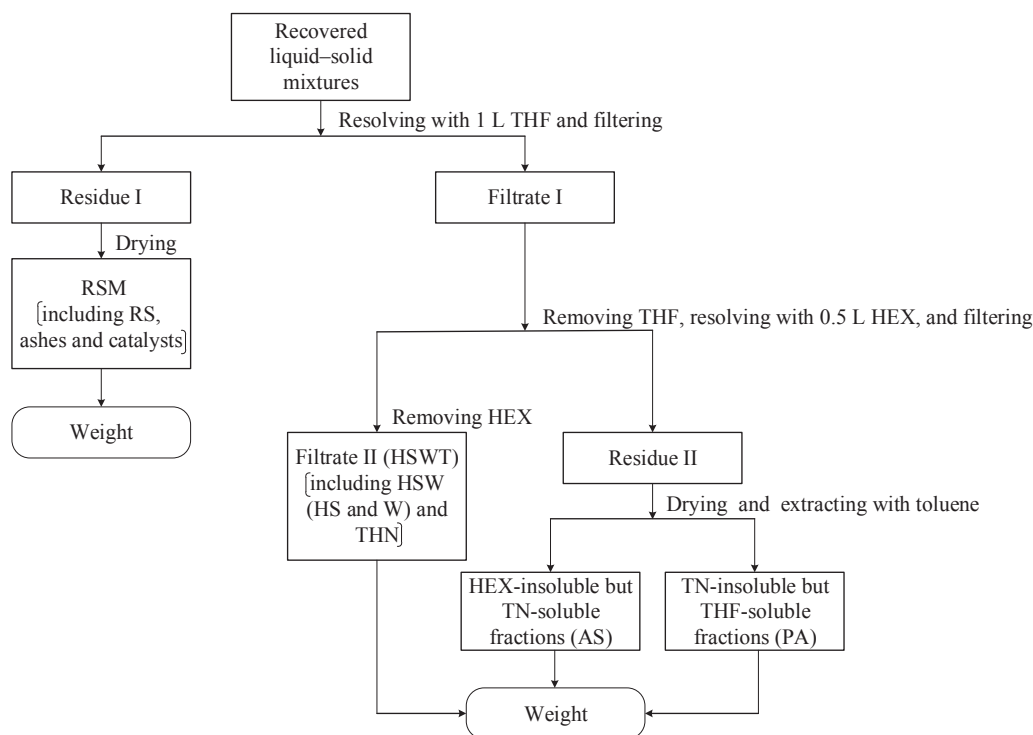


Fig. 1. Procedures for separation of recovered liquid-solid mixtures from each liquefaction experiment.

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