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Comparative evaluation of different non-condensable gases on thermal behaviors, kinetics, high pressure properties, and product characteristics of heavy oil

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ABSTRACT

In this work, the thermal behaviors, kinetic parameters, high pressure properties, and product characteristics of Qi 40 heavy oil in air, nitrogen, carbon dioxide, oxygen-denuded air, and flue gas atmospheres were systematically and comparatively studied by thermogravimetric analysis, kinetic analysis, pressure-volume-temperature test, and stimulation experiments. The thermal decomposition of heavy oil occurred in three major zones. The comprehensive devolatilization indices of heavy oil in nitrogen, carbon dioxide, oxygen-denuded air, air, and flue gas atmospheres were 3.32×10^{-7}, 2.94×10^{-7}, 2.07×10^{-7}, 2.30×10^{-7}, and $2.58 \times 10^{-7}\% \, K^{-3} \, min^{-2}$, respectively. The kinetics analysis indicated that, except for zone 2 in oxygen-denuded air, the best kinetic models of three zones were $(1-x)^{1/3}$, $(1-x)^{3/4}$, and $(1-x)$, respectively. Pressure-volume-temperature tests displayed that the high pressure properties of heavy oil were mainly influenced by the gas solubility effects at low temperatures, and the heating effects at high temperatures. Moreover, Fourier transform infrared spectra, crude oil group, element, and gas chromatography analysis on products from stimulation experiments of heavy oil all showed that the product characteristics might be influenced by the existence of oxygen in the non-condensable gases. The results of this study provided useful information for potential application of non-condensable gases injection on thermal enhanced oil recovery.

1. Introduction

Along with the continuous development of the global economy, the rapid growth of energy demand prompted the exploitation of new possible petroleum resource. As an alternative energy resource, heavy oil has attracted a wide attention in recent years for its huge reserves all over the world [1]. Feasible exploitation techniques have been widely developed for heavy oil recovery [2]. Because of some special properties of heavy oil, including high density, high viscosity, and poor fluidity, thermal recovery seems to be one of the most potential ways [3]. Among various thermal enhanced oil recovery techniques, steam stimulation and steam flooding are the two most popular methods [4]. The practices in the steam exploitation have proven that the advantages are obvious in the early stage, but the water cut will rise rapidly after multi-run injection. Recently, concerns over the adverse influences in the steam mining later period have led investigators to make great efforts in heavy oil production by thermal recovery assisting with non-condensable gas injection [5]. Compared to heavy oil recovery by steam injection, gas injection can effectively reduce heat loss and get a lager sweep volume [6].

Heavy oil recovery by non-condensable gas injection is an effective technique to enhance oil recovery (EOR) [7]. It eventually utilized the energy carried by the non-condensable gas with a high temperature to heat heavy oil reservoir, reduce oil viscosity, and improve oil fluidity in the porous rocks [8]. As several typical gases, nitrogen (N_2), carbon dioxide (CO_2), flue gas, and air were considered in heavy oil production for extensive sources, low cost, and good oil recovery [9]. In the literature [10], the dissolving capacity and viscosity reducing effect of CO_2 on heavy oil have been compared with those of N_2, and found that CO_2 was much more effectively. CO_2 can recover more oil via the generation of miscibility by lowering the interfacial tension (IFT) [11]. Generally, to realize the target of EOR, the gas should be preheated to the certain temperature on the ground. From the viewpoint of energy conservation, the flue gas with high temperature has been popularly used as a thermal fluid to increase heavy oil recovery [12]. Further, to avoid the heat loss in the gas transmission, injecting air to the oil reservoir was brought into operation, and EOR was achieved mainly due to the steam flooding and viscosity reduction as a result of heat

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Nomenclature

EOR	enhance oil recovery
ISC	in-situ combustion
IFT	interfacial tension
DSC	differential scanning calorimetry
DAEM	distributed activation energy model
TG	thermogravimetry
TGA	thermogravimetric analyze
DTG	differential thermogravimetry
FTIR	Fourier transform infrared spectrometer
SARA	saturate, aromatics, resin, and asphaltene
GC	gas chromatography
TCD	thermal conductivity detector
PVT	pressure-volume-temperature
T_i	initial decomposition temperature, K
T_p	peak temperature of each zone, K
T_f	final decomposition temperature, K
$-R_\mathrm{p}$	maximum weight loss rate of each zone, % min^{-1}
$-R_\mathrm{v}$	average weight loss rate of each zone, % min^{-1}
ΔT	temperature range at half value of $-R_\mathrm{p}$, K
WL	weight loss percentage of each zone, %
W_r	residual weight after experiment, %
D	comprehensive devolatilization index, % $\mathrm{K}^{-3}\,\mathrm{min}^{-2}$
R	universal gas constant, $\mathrm{J\,mol^{-1}\,K^{-1}}$
dx/dt	conversion rate, % min^{-1}
E	activation energy, $\mathrm{kJ\,mol^{-1}}$
A	pre-exponential factor, s^{-1}
β	heating rate, $\mathrm{K\,min^{-1}}$
$k(T)$	rate constant
T	absolute temperature, K
x	conversion degree, %
$f(x)$	differential kinetic model
$g(x)$	integral kinetic model
P	pressure, MPa
V	volume, mL
Z	compressibility factor
n	mole, mol
S	solubility, $\mathrm{m^3\,m^{-3}}$
VR	volume ratio, $\mathrm{m^3\,m^{-3}}$
R^2	correlation coefficient
C	carbon
H	hydrogen
O	oxygen
N	nitrogen
S	sulfur
O_2	oxygen
N_2	nitrogen
CO_2	carbon dioxide
CH_4	methane
H_2	hydrogen
$-CH_3$	methyl
$-CH_2$	methane
C=O	carbonyl
−OH	hydroxyl

produced by the in-situ combustion (ISC) of crude oil [13]. As pointed out by Fan et al. [14], almost all the oxygen (O_2) in the injection gas was consumed by the low-temperature oxidation of heavy oil, which could effectively avoids the O_2 breakthrough and consequently safety issues during the air injection process. But in fact, the combustion process of heavy oil in the reservoir is difficult to be monitored, so that the O_2 breakthrough does exist. In this case, the O_2 addition reactions between crude oil and O_2 remaining in gas would result in a dramatic increase of the oil viscosity with the formation of heavier oil fractions [15]. Additionally, the air injected with a high O_2 would make the combustion process uncontrollable, and a large number of petroleum resources were also wasted. To gain a good heavy oil recovery, using O_2-denuded air as gas injection might be a nice choice. Given the above, air, N_2, CO_2, flue gas, and O_2-denuded air could be chosen as thermal fluids to improve heavy oil recovery.

To date, a number of studies have been performed on the thermal behaviors, kinetics, phase properties, and products characterization using heavy oil as feedstock. Kok and Gundogar [16] have studied the thermal behaviors of Turkish crude oils in air and N_2 atmospheres via differential scanning calorimetry (DSC). From DSC curves, the combustion process of Turkish oils could be divided into two zones of the low temperature oxidation and high temperature oxidation, and the pyrolysis process occurred in two zones of the distillation and cracking. Kok [17] studied thermal kinetics of heavy oil by thermogravimetric analyzer (TGA) at distinct heating rates. It was found that activation energies generated for the high temperature oxidation region were in the range of 48.5–151.0 $\mathrm{kJ\,mol^{-1}}$ at three different heating rates. In the study of Fan et al. [18], the thermal oxidative decomposition kinetics of heavy oil were analyzed by the distributed activation energy model (DAEM). It was observed that the apparent activation energies at low temperatures were around 100 $\mathrm{kJ\,mol^{-1}}$, and at high temperatures were about 190–230 $\mathrm{kJ\,mol^{-1}}$. With regard to the phase properties, Riyahin et al. [19] presented a new set of correlation for estimating crude oils properties based on some experimental pressure-volume-temperature (PVT) data. It was found out that the new correlations were more accurate than the other ones. Cao and Gu [20] evaluated the effects of temperature on the phase property, mutual interactions, and oil recovery of a light crude oil-CO_2 system. It was found that the saturation pressure and oil-swelling factor increased almost linearly with CO_2 concentration. As for products characterization, Pu et al. [21] have detected the content of O_2, CO_2, CO, and hydrocarbon gas (C_1-C_6) of the produced gases from the low temperature oxidation of heavy oil. Khansari et al. [22] performed product estimation for the low temperature oxidation of Lloydminster heavy oil. The elemental analysis on reaction residues suggested that aldehyde, alcohols and ketones, hydroperoxide and carboxylic acids, ketones and hydro-peroxide are the major products of the first, second, third, and fourth subzone, respectively. Yang et al. [23] have made a comprehensive analysis of the properties of crude oil in oxidation experiments, and found that the intermediate components (C_7–C_{17}) made a great contribution to crude oil cracking. Although the thermal behaviors, kinetics, phase properties, and product characteristics of heavy oils have been reported, previous studies were just carried out under N_2, CO_2, or air condition.

In view of these, the thermal behaviors, kinetic parameters, high pressure properties, and product characteristics of heavy oil in air, N_2, CO_2, oxygen-denuded air, and flue gas were systematically and comparatively evaluated. The knowledge obtained from this work could present some basic information for potential application of non-condensable gases on thermal enhanced oil recovery.

2. Materials and methods

This section gave a detailed introduction for the heavy oil sample, non-condensable gases, thermal analysis method, kinetic theory, pressure-volume-temperature (PVT) test device and method, and non-condensable gas stimulation experiments.

2.1. Raw materials

The heavy oil sample studied in this work was selected from Qi 40