

Participation of methane in economically and environmentally favorable catalytic asphaltene upgrading process

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Supplementary Information

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Asphaltene preparation

Typically, 5 grams of bitumen sample (Alberta) was first dispersed in heptane with vigorous stirring. Next, the suspension was put on a medium rate filter paper and set up in a Soxhlet extractor. Heptane was then refluxed at high temperature to remove all heptane-soluble in the oil sample from the filter paper. After that, the sample in filter paper was fully desiccated in the oven at 90 °C and set up again in the Soxhlet extractor. Toluene was then refluxed at high temperatures to extract all soluble substances, which were determined to be asphaltenes. After the asphaltene in toluene solution was obtained, it was further calibrated to the asphaltene content of 10 wt% by adding or evaporating a certain amount of toluene.

Catalyst preparation and characterization

The HOU catalyst, which is specifically designed for application of heavy oil upgrading, is prepared as follows. First, NH₄-ZSM5 with a STA (silica to alumina) value of 23 was purchased from Zeolyst USA. The zeolite was converted into HZSM5 through calcination at 600 °C in air atmosphere for 5 hours. Next, the metal-modified HZSM-5 catalyst was prepared by a stepwise impregnation method. In this method, metal precursors including AgNO₃ (Alfa Aesar, 99.9%), Ga(NO₃)₃·xH₂O (Alfa Aesar, 99.9%), Ce(NO₃)₃·6H₂O (Alfa Aesar, 99.9%), (NH₄)₆Mo₇O₂₄·4H₂O (Alfa Aesar, 99.9%) and Co(NO₃)₂ (Alfa Aesar, 99%) were first prepared as aqueous solution. The mass loadings of each metal species over the ZSM5 support were 10 wt%, 7 wt%, 5 wt%, 1 wt%, 1 wt% for Mo, Co, Ce, Ag, Ga respectively. All metals were in elemental form for the loading calculation. Then, the zeolite support was added in each solution, respectively, followed by a desiccation process in the oven at 105 °C for 2 hours and a calcination process at 550 °C for 3 hours in air atmosphere with a temperature ramping rate of 10 °C min⁻¹. The final catalyst (labelled as HOU-fresh) was a fine powder with grayish color and stored in well-closed vials for subsequent use.

After the reaction, the catalyst covered by coke was collected and labelled as HOU-used. The used catalyst was calcined at 800 °C for 2 hours under air atmosphere with a temperature ramping rate of 10 °C min⁻¹ to fully remove the formed coke. The produced catalyst is labelled as HOU-regenerated. A reaction with the regenerated catalyst was also carried out and the data were compared with entry 1. The asphaltene conversion decreases (-5.1%) as well as the light fraction yield (-10.4%), while the coke formation increases (5.4%), indicating the performance of catalyst cannot be fully recovered. This can be due to the sintering of active components during the regeneration process for coke combustion. However, the regeneration process can be further optimized (such as temperature optimization, choosing better gas environment, etc.) to get a better catalyst reusability.

N₂ adsorption-desorption analysis of catalysts were carried out on ASAP 2020 Plus surface area and porosimeter system (Micromeritics). The sample was first degassed at 350 °C for 4 hours with a temperature ramping rate of 10 °C min⁻¹ and a vacuum level of 20 μmHg. Then the analysis was performed in liquid nitrogen to get a 56-point adsorption-desorption isotherm. The total surface area was calculated by BET method and the total pore volume was calculated at 0.995 relative pressure. Micropore surface area and volume were obtained by t-plot method, and average pore size was acquired using BJH method. The results are shown in Fig. S1 and Table S1. It can be observed that the surface

area and pore volume of the regenerated catalyst is similar to those of the fresh catalyst, indicating the physical structure of the catalyst can be successfully restored after regeneration. The used catalyst demonstrates a higher surface area and larger average pore size probably due to the formation of amorphous coke.

X-ray diffraction (XRD) spectra of the catalysts were performed on a Rigaku ULTIMA III X-ray diffractometer. The radiation source was Cu K α and the tube voltage and current were 40 kV and 44 mA respectively. The scanning range of 2θ was $3\sim 90^\circ$ with a scanning rate of 3° min^{-1} . The results are shown in Fig. S2.

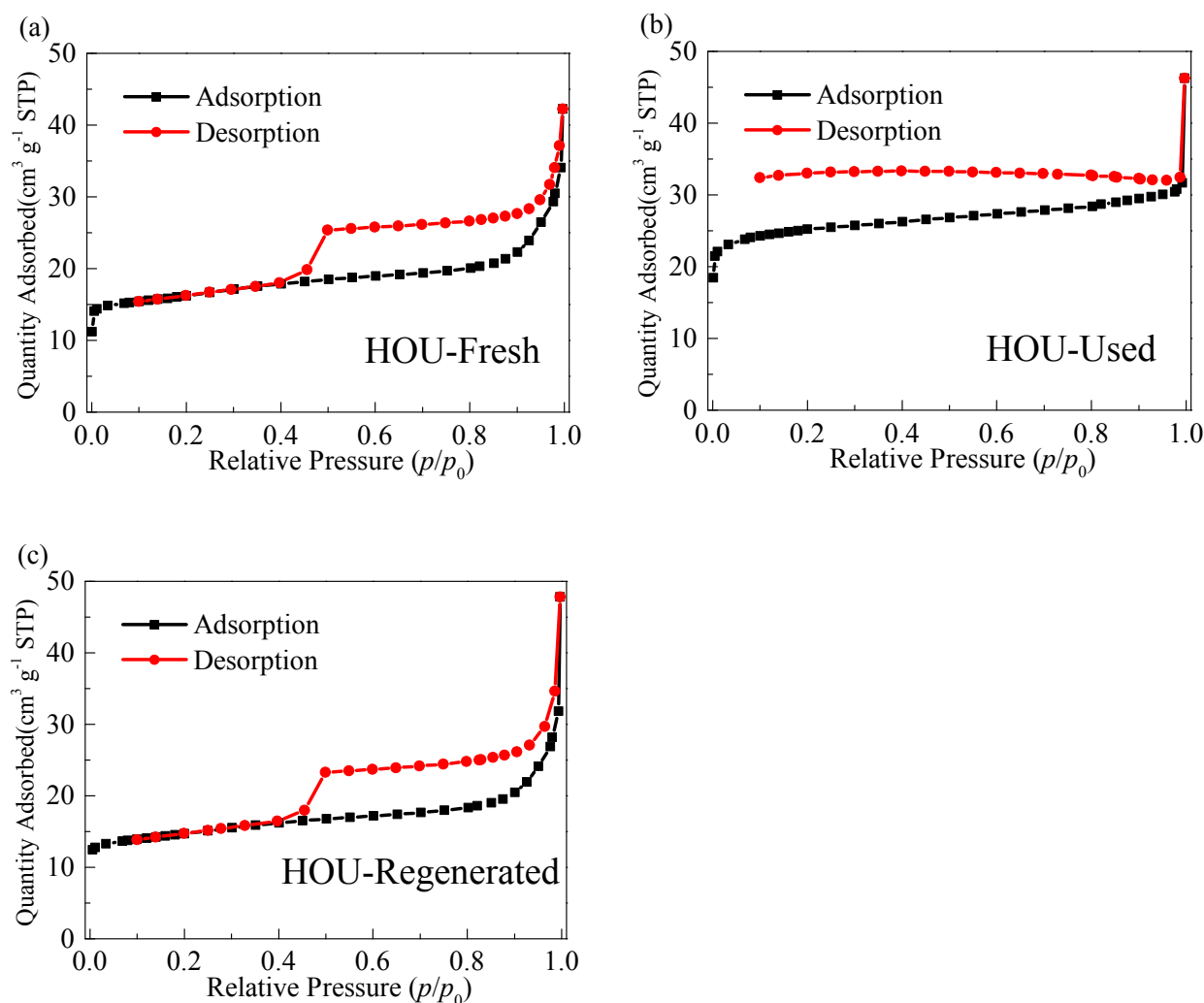


Fig. S1 N_2 adsorption-desorption isotherms of catalyst samples.

Table S1 Surface and porous properties of catalyst samples.

Sample	HOU-fresh	HOU-used	HOU-regenerated
Total surface area ($\text{m}^2 \text{g}^{-1}$)	53 \pm 1	81 \pm 2	49 \pm 1
Micropore area ($\text{m}^2 \text{g}^{-1}$)	35	48	30
Total pore volume ($\text{cm}^3 \text{g}^{-1}$)	0.047	0.048	0.043
Micropore volume ($\text{cm}^3 \text{g}^{-1}$)	0.017	0.030	0.015
BJH average pore size (nm)	8.20	11.14	8.30

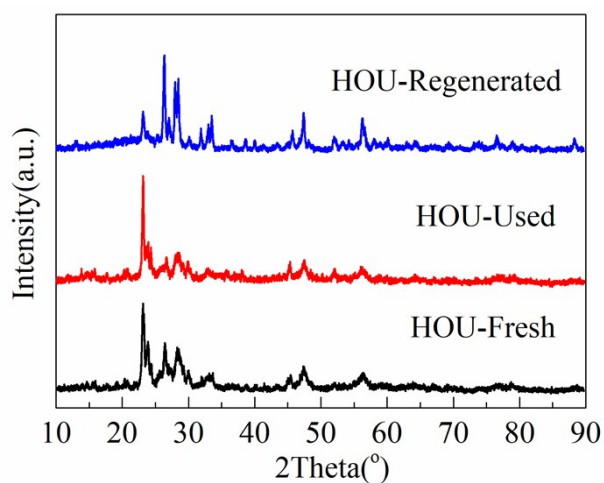


Fig. S2 XRD patterns of catalyst samples.

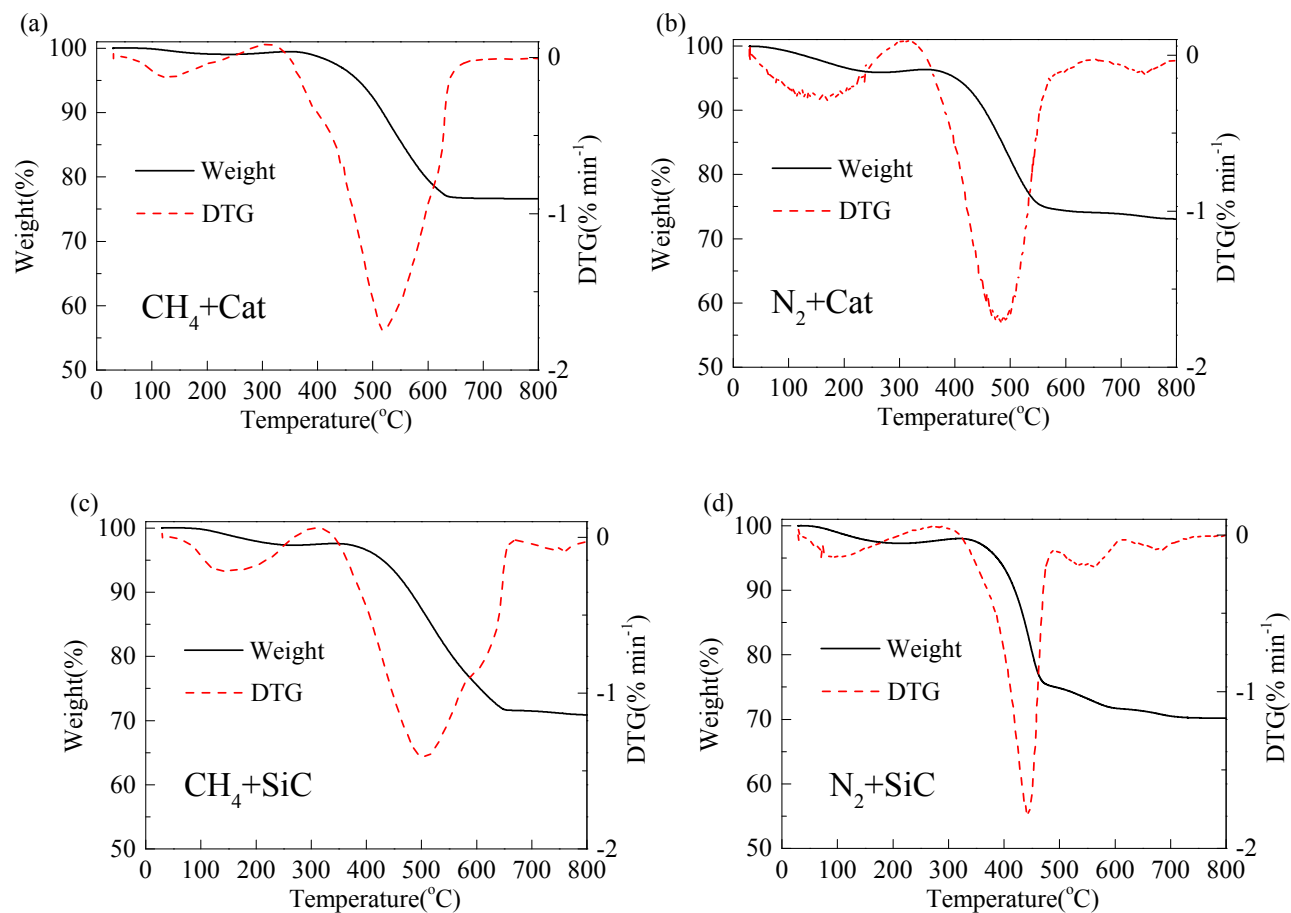


Fig. S3 Thermalgravimetric analysis (TGA) curves of solid after reaction from entry 1~4. (a) entry 1, (b) entry 2, (c) entry 3, (d) entry 4.

Reaction process

The reaction conditions were carefully selected after optimization. For temperature dependence, a lower temperature of 350 °C led to limited asphaltene conversion (less than 10%), while a higher temperature of 450 °C led to severe coking process (more than 90% coke yield). For reaction time, the 0.5 h reaction led to 67% asphaltene conversion, which was significantly less than that in 1 h reaction (89%). However, further extension of reaction time to 2 h provided limited improvement on asphaltene conversion (93%). For asphaltene concentration, a reaction with lower asphaltene concentration of 7 wt% was carried out and similar results were observed (90% asphaltene conversion). 10 wt% is close to the asphaltene content in industrial bitumen samples and it was thus selected to mimic the real upgrading processes and make fully use of the catalyst's catalytic capacity. Meanwhile, the concentration cannot go too high due to the solubility limitation of asphaltene in toluene solvent. For catalyst to asphaltene mass ratio, an experiment with catalyst : asphaltene = 1:10 was carried out. However, the performance was much poorer. Only 51% asphaltene conversion was observed and the coke selectivity was 53%, which was 11% higher than that in entry 1. It is supposed that the excessive asphaltene fully covered the catalyst in this case due to its strong adhesion ability. Therefore, the majority of methane molecules cannot get contacted with the catalyst and activated, leading to the unfavorable results. Therefore, 400 °C, 1 h, 10 wt% asphaltene concentration and catalyst to asphaltene ratio of 1:1 were adopted throughout the study.

A typical upgrading experiment was performed as follows. First, 20 grams of asphaltene solution (contains 2 grams asphaltene in toluene) was added in a 300 mL batch reactor manufactured by Parr Instrument USA, which can be used at high temperature up to 500 °C and high pressure up to 2000 psi (13.8 MPa). Then, 2 grams of catalyst (HOU) was added and the ratio of asphaltene to catalyst was fixed to be 1:1. The large amount of catalyst was used to guarantee the surface of catalyst will not be fully blocked by asphaltene and coke during the reaction process so that methane participation could be considerably enhanced. Then, the reactor was sealed with a multi-function flanged top equipped with stirrer, thermocouple, and seal flush cooling water system. Next, nitrogen was used to purge the reactor through connected tubing and acts as an inert internal standard during the process with a pressure of 0.8 MPa. Methane was introduced subsequently from gas cylinder through connected tubing to a pressure of 3.5 MPa (methane pressure 2.7 MPa). After leak test, during which the reactor weight and pressure was confirmed to be stable, the reactor was put into a temperature-controlled mantle for the duration of the

reaction. The temperature and pressure change during the reaction process was recorded by videos and the curve was shown in Fig. S4. The reaction lasted for 1 hour after the 400 °C set-point was achieved. After the reaction, the reactor was cooled down by external air flow at room temperature.

A series of control experiments were also carried out. The first control experiment, which was labeled as entry 2 (N₂+Cat), adopted the similar reaction conditions as described in entry 1 except that no methane was introduced before the reaction. Instead, nitrogen was directly introduced to a pressure of 3.5 MPa. In the second control experiment (entry 3, CH₄+SiC), the similar reaction conditions as described in entry 1 was adopted while the catalyst was replaced by same amount of SiC, an unreactive solid substrate material. The third control experiment (entry 4, N₂+SiC) used both 3.5 MPa N₂ as the feeding gas and SiC as the solid in the reaction, in order to investigate the thermal cracking evolution with an unreactive solid substrate during the upgrading process.

Performance evaluation

After each reaction, gas, liquid, and solid phase products were analyzed respectively, in the following manner. (1) Gas phase: the product gas was directly fed into a micro-chromatography (micro-GC 490, Agilent) to analyze the yield of hydrogen and C₁~C₅ hydrocarbons. First, the GC was calibrated by possible gases including H₂, N₂, C₁~C₅ alkanes and C₁~C₅ alkenes and the mole fraction was correlated with the peak area in the chromatogram. Therefore, after the GC analysis of product gas, the mole fraction of each component can be obtained. Besides, the overall mass of gas was also calculated by the difference of the whole reactor system's mass before and after degassing process. Finally, the mole fraction of each species was converted into mass fraction according to the molecular weight and the mass of each gas product was calculated by multiplying its mass fraction by the total mass of gas product. (2) Liquid phase: the liquid phase was collected and an real distillation process was performed to determine the different fractions in liquid product. The gasoline fraction was collected as the distillate up to 180 °C at atmospheric pressure. It is proved that the gasoline fraction only contains the products derived from toluene solvent (Fig. S6 and Table S3). Therefore, the gasoline part was not considered for the calculation of asphaltene product distribution. Meanwhile, it is also proved that the fractions heavier than gasoline only contains the products derived from asphaltene (Table S2), and the content of each part was determined by the following method. First, after gasoline fraction was removed, the diesel fraction was collected as the distillate up to 225 °C at an absolute pressure of 15 kPa provided by a vacuum pump. Next, heptane was added to the remaining liquid under vigorous stirring to form a suspension. The suspension was then put on a medium rate filtering paper and rinsed by heptane for another three times. The filtrate was fully desiccated in the oven at 80 °C and the weight was recorded. This heptane-soluble part was defined as medium distillate in the following study. After that, the sample in filtering paper was also fully desiccated in the oven at 80 °C and the weight was collected. This heptane-insoluble part was defined as heavy residue in the following study. (3) Solid phase: the solid product was subjected to thermogravimetric analysis (TGA) to determine the amount of coke formation during the process. TGA measurement was performed with a simultaneous thermal analyzer (PerkinElmer STA 6000). The samples were held at 30 °C for 5 min for a stable initial weight, then ramped to 800 °C at a rate of 20 °C min⁻¹ under 30 mL min⁻¹ air flow and held for 5 min. The weight loss from 350 °C to 800 °C was attributed to the coke oxidation (Fig. S3).

The mass of gas, liquid, and solid phases before and after reaction were also recorded. After data collection, the corresponding values were calculated by the following equations:

$$\text{Overall Mass Balance} = \frac{\text{mass of (gas+liquid+solid) after reaction}}{\text{mass of (gas+liquid+solid) before reaction}} \times 100\%$$

$$\text{Asphaltene Mass Balance} = \frac{\sum \text{mass of products}}{\text{mass of feed asphaltene}} \times 100\%$$

$$\text{Asphaltene Conversion} = \left(1 - \frac{\text{mass of remaining asphaltene after reaction}}{\text{mass of feed asphaltene}}\right) \times 100\%$$

$$\text{Light Fraction Yield} = \frac{\text{mass of heptane-solubles in product}}{\text{mass of feed asphaltene}} \times 100\%$$

$$\text{Light Fraction Selectivity} = \frac{\text{mass of heptane-solubles in product}}{\text{mass of converted asphaltene}} \times 100\%$$

$$\text{Coke Yield} = \frac{\text{mass of coke in product}}{\text{mass of feed asphaltene}} \times 100\%$$

$$\text{Coke Selectivity} = \frac{\text{mass of coke in product}}{\text{mass of converted asphaltene}} \times 100\%$$

$$\text{Liquid Yield} = \frac{\text{mass of liquid product}}{\text{mass of feed asphaltene solution}} \times 100\%$$

$$\text{Methane Conversion} = \left(1 - \frac{\text{mole of remaining methane after reaction}}{\text{mole of feed methane}}\right) \times 100\%$$

Liquid product analyses

Simulated distillation analysis

Due to the limitations of real distillation for heavy components in the study, simulated distillation analysis (SDA) was also carried out on an Agilent 8890 GC system equipped with a 30 m HP-5 column and an FID detector. The results were analyzed by SimDis Expert software from Separation Systems to get the boiling curves of oil samples. Liquid nitrogen was used to realize the cryogenic GC analysis from -20 °C to 450 °C with a ramp rate of 10 °C min⁻¹.

Nuclear magnetic resonance

¹³C liquid nuclear magnetic resonance (NMR) analysis was conducted at 9.4 T ($\nu_0(^{13}\text{C}) = 100.6$ MHz) on a BRUKER AVANCE III 400 NMR spectrometer with a BBFO probe. 1000 scans were performed to get the spectra with a spectral width of 24 kHz. Deuterated chloroform (CDCl₃) was used as the solvent and the chemical shift was calibrated by the peak of carbon in CDCl₃ at 77.3 ppm.

Total acid number

The total acid number (TAN) of liquid product was measured by a Metrohm 848 Titrino Plus titrator. The sample was first dispersed in the titration solution (toluene and propanol with 0.5 wt% water) and 0.1 mol L⁻¹ KOH was added continuously until the sudden change of voltage measured by a pair of electrodes was detected. The TAN was then calculated according to the consumed volume of KOH solution.

Sulfur content

The sulfur content was measured by inductively coupled plasma-optical emission spectrometry (ICP-OES) collected by iCAP 7000 SERIES ICP spectrometer (Thermo Scientific). The sample was first dispersed in PermiSolv™, which is a standard solvent for oil analysis. Then, the solution was measured at least three times and the sulfur content in original sample was calculated by multiplying the dilution factor.

Matrix-assisted laser desorption/ionization

Matrix-assisted laser desorption/ionization (MALDI) was conducted on Autoflex III Maldi-TOF

instrumentation with time of flight (TOF) mass spectrometer (Bruker). 2,5-dihydroxybenzoic acid (DHB) was used as matrices and the laser was generated by a Smartbeam laser system.

Toluene blank reaction

The toluene blank reaction (entry 0) was performed as follows. 20 grams pure toluene and 2 grams HOU catalyst were fed into the reactor and the similar reaction procedure described in reaction process section was followed.

The change of temperature and pressure during the blank test (entry 0) is shown in Fig. S4. It should be noted that the temperature and pressure curves in other entries (entry 1~4) followed the similar pattern with a deviation of less than 5 °C and 2 bar, proving the good repeatability of the temperature and pressure control during the process. According to Fig. S4, a unique temperature drop during the reaction process was observed, and meanwhile the pressure remains unchanged. Consulting the phase diagram of toluene (Fig. S5), the anomalous stage in temperature and pressure curves can be attributed to the phase transition of toluene from liquid into supercritical fluid during the process. In general, the phase transition towards supercritical fluid is highly endothermic and thus the temperature decrease can be explained. It is worth noting that in the supercritical phase, the physical properties of substances change remarkably, which could be favorable for the reaction. For example, the density and viscosity of toluene will drop considerably during the stage, and the diffusivity will be increased correspondingly, facilitating the mass and heat transfer of the reaction. In addition, there is no surface tension in a supercritical fluid, as there is no liquid-gas phase boundary, favoring the contact among the gaseous methane, the reactant in liquid phase and the solid catalyst. Furthermore, by changing the pressure and temperature of the fluid, the properties can be “tuned” to be more liquid-like or more gas-like. The relatively easy realization of toluene in supercritical phase makes it a promising solvent for the upgrading process of heavy oil feedstocks.

The gas phase product of the blank test (entry 0) is shown in Table S4 to compare with the main reaction (entry 1) and the liquid phase analysis is shown in Table S3. According to Table S4, only little amount of gas was produced during the reaction and the gas product distribution was quite similar in entry 0 and entry 1, indicating the gas phase product is produced only from the toluene solvent. However, a significant increase of methane conversion was observed, indicating the participation of methane in asphaltene upgrading process. The incorporation of methane in asphaltene reaction is highly valuable since the excessive H in methane can be used to compensate the high C:H ratio in asphaltene and more valuable product can be anticipated.

According to Table S3, a considerable conversion of toluene was observed and the majority of the

products consisted of benzene and xylene, indicating the exchange of side chain methyl group is predominant during the reaction. Other reactions, such as the ring cleavage, isomerization and hydrogenation were insignificant under current conditions. Besides, no coke formation was detected as a solid product during the process. Therefore, it is reasonable to use toluene as the solvent for further study of heavy oil components due to the simplicity of the background reaction.

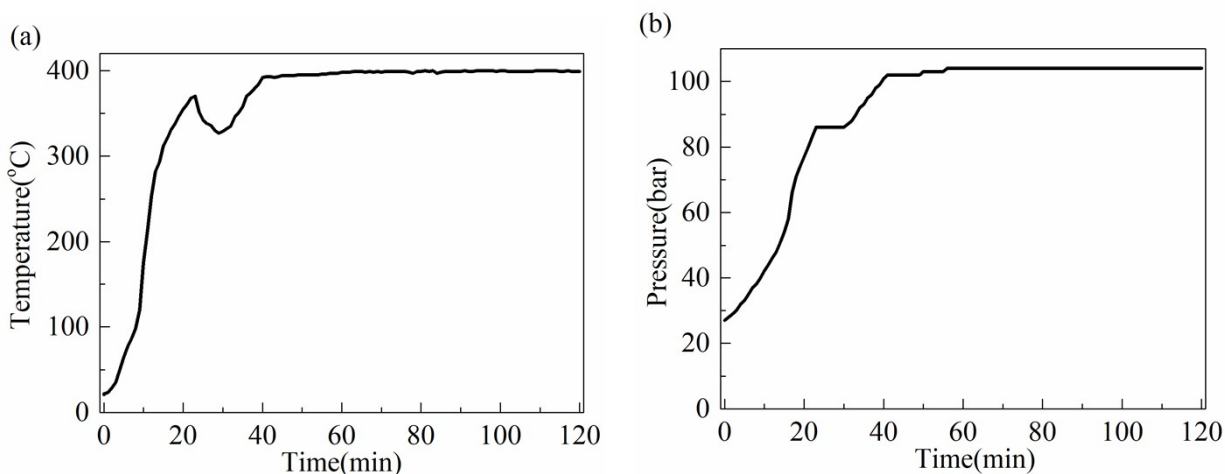


Fig. S4 Typical curve of (a) temperature and (b) pressure during the asphaltene upgrading reaction process.

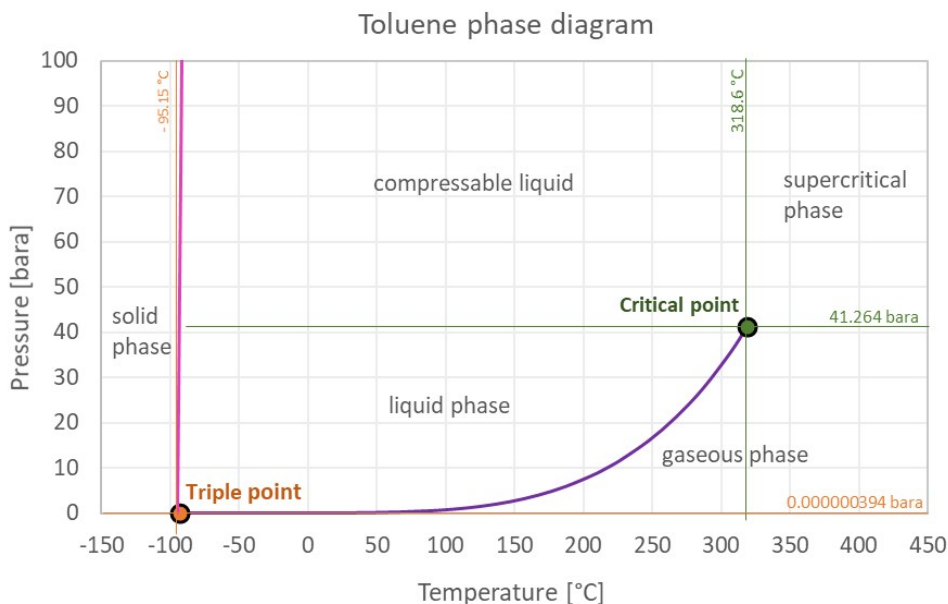


Fig. S5 Phase diagram of toluene. Source: www.engineeringtoolbox.com.

Table S2 Overall liquid product distribution from entry 0 (toluene blank test) and entry 1 by actual distillation. No product heavier than gasoline was detected in entry 0. Therefore, the emergence of these fractions can be totally attributed to asphaltene products.

Entry	Gasoline	Diesel	Medium distillate	Heavy residue
0	100	0	0	0
1	94.45	1.16	3.28	1.11

Table S3 GC-MS analysis of gasoline product distribution from entry 0 (toluene blank test) and entry 1, all values are based on mole percentages. Significant difference of product distribution was observed. The toluene conversion as well as the selectivity for Benzene and xylenes were slightly lower in entry 1 because the catalyst was partially covered by asphaltene and coke during the reaction process, impeding the toluene conversion. It was proved that all gasoline species are derived from toluene solvent and no asphaltene products get involved.

Entry	Sum of BTX (%)	Toluene conversion (%)	Benzene selectivity (%)	Xylenes selectivity (%)		
				p-xylene	m-xylene	o-xylene
0	99.81	16.06	43.90	18.06	13.45	7.29
1	99.98	13.36	47.75	15.42	10.63	6.06

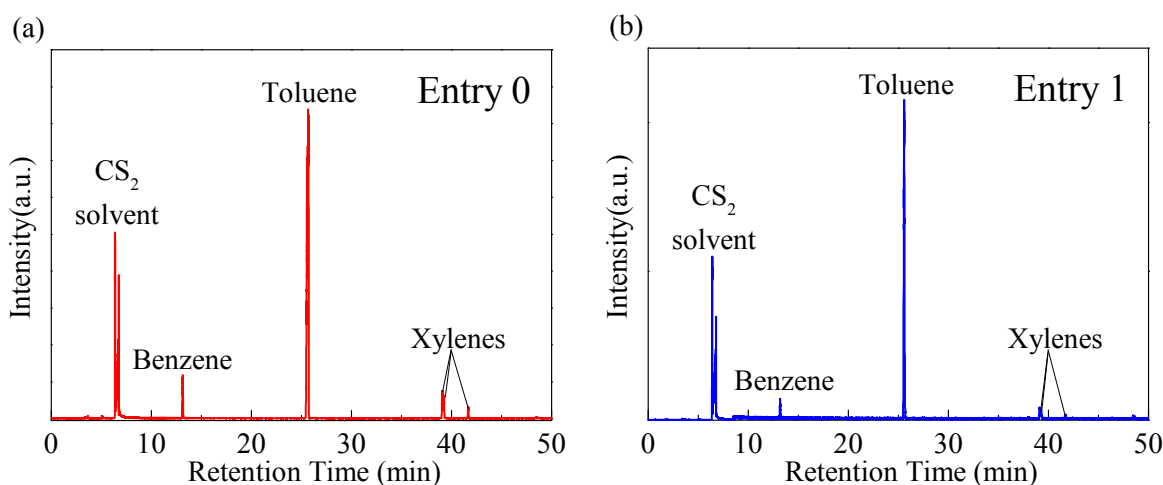


Fig. S6 Gas chromatograph-mass spectrometer (GC-MS) chromatogram of gasoline product from entry 0 (toluene blank test) and entry 1. Instrument and analysis conditions: GC-MS, PerkinElmer GC Claus 680 and MS Clarus SQ 8T) equipped with a paraffin-olefin-naphthene-aromatic (PONA) column (Agilent HP-PONA). The oven temperature of the GC was programmed to hold at 35 °C for 15 min, ramp to 70 °C at 1.5 °C min⁻¹, ramp to 150 °C at 3 °C min⁻¹ and hold for 30 min, then ramp to 200 °C at 10 °C min⁻¹. The amount of each component was calibrated by standard chemicals including alkanes, olefins and aromatics with different carbon numbers. Identification of the species was achieved by comparing the obtained mass spectra with those in the system's database (NIST).

Table S4 Gas chromatography (GC) analysis of the gas products from entry 0 (toluene blank test) and entry 1 (CH₄+Cat). Instrument and conditions: GC, four-channel micro-GC (490, Agilent) equipped with thermal conductivity detector (TCD). Columns for each channel: 10 m molecular sieve 5A column in first channel, 10 m PPU column in second channel, 10 m alumina column in third channel and 8 m CP-Sil 5CB column in fourth channel. Temperature and pressure of columns: 80 °C and 200.0 kPa (first), 100 °C and 175.0 kPa (second), 80 °C and 180.0 kPa (third), 100 °C and 85.0 kPa (fourth), analysis time: 3 min. The carrier gas was Ar and N₂ was used as an internal standard to calculate the methane conversion in each reaction.

Entry	Methane conversion (%)	H ₂ yield (wt%)	C ₂ yield (wt%)	C ₃ yield (wt%)	C ₄ yield (wt%)	C ₅ yield (wt%)
0	2.7	0.20	0.61	0.03	0.01	0
1	7.4	0.15	0.60	0.02	0.02	0