



Chemical Synthesis of Fuel Hydrocarbon from CO₂ and Activated Water, and Purification of Commercial Light Oil for Dream Oil

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Abstract

Here we show that petroleum can be formed efficiently at normal temperatures and pressures from carbon dioxide and activated water. The CO₂ nano-bubble containing water was treated with photocatalyst in the presence of oxygen under UV irradiation. The activated water was mixed vigorously with kerosene or light oil to form an emulsion. The emulsion gradually separated into a two-phase solution. After phase separation, the volume of kerosene or light oil, depending on which oil was utilized, increased by 5 to 10%. Likewise tetradecane was used, and original tetradecane may be used as a template for the synthesis of new tetradecane. When commercial light oil was treated in the same way, most organic and inorganic impurities were removed from the oil and very clean light oil was obtained. We named it as dream light oil. The dream light oil meets strict Japanese Industrial Standards (JIS).

Keywords: Fuel hydrocarbon production, CO₂, Activated water, Photocatalyst, Purification of commercial oil.

Abbreviations: JIS-Japanese Industrial Standards, C₆-Hexane, C₈-Octane, C₉-Nonane, C₁₀-Decane, C₁₁-Undecane, C₁₂-Dodecane, C₁₃-Tridecane, C₁₄-Tetradecane, C₁₅-Pentadecane, C₁₆-Hexadecane, C₁₇-Heptadecane, C₁₈-Octadecane, C₁₉-Nonadecane, C₂₀-Icosane, C₂₁-Henicane, C₂₂-Docosane, C₂₃-Tricosane, C₂₄-Tetracosane, C₂₅-Pentacosane, C₂₆-Hexacosane, C₂₇-Heptacosane.

Introduction

Both biotic and abiotic oil hypotheses have been proposed to explain the origin of oil on our planet. Supporting the abiotic oil hypothesis, it has been known since 1967 that petroleum could be formed at high temperatures and pressures from inorganic carbon in the form of carbon dioxide with hydrogen or methane. The abiotic origin of petroleum has been reviewed in detail by Glasby, who raises a number of objections, including that there is no direct evidence to date of abiotic petroleum [1]. Geologists now consider the abiotic formation of petroleum scientifically unsupported, and they agree that petroleum is formed from organic material [1].

However, some argue that the abiotic theory cannot be dismissed because the mainstream theory has yet to be established conclusively [2]. In 1920's, Fischer-Tropsch process was reported indicating that petroleum can be produced from CO and H₂ with special catalyst under high pressures and high temperatures. Since then, no apparent procedures on the topics have been exploited [3]. Here, we show that petroleum can be formed efficiently at normal temperatures and pressures from carbon dioxide and activated water. In addition, purification of commercial light oil (removal of organic and inorganic impurities) is presented.

Materials and Methods

Generation of Activated Water

Tap water passed through reverse osmosis membrane (Toray Industries, Inc., Osaka, Japan) to get pure water. Then CO₂ gas was supplied into the water by nano-bubble generator (Nishiken-devis, Osaka) for 30 min. The nano-bubbles are generally maintained in the water for a long period of time unless CO₂ is consumed. The nano-bubble containing water was treated in the presence of oxygen gas with TiO₂ catalysis (Takemoto Industry, Okayama, Japan) under irradiation of UV light {UV sterilization lamp: Panasonic GL-40 40w (254nm) and Black light: Toshiba FL40S BLB 40w (315nm-400nm, peak wave length 352nm)} for 30min.

Material and quantity of photocatalyst is shown below. UV-reactive TiO₂ (70g), visible light-reactive TiO₂ powder (70g) (Ishihara Sangyo Kaisha, Ltd., Osaka, Japan), iron powder No. 300 (10g) (Wako Pure Chemical Industries, Ltd., Osaka), platinum powder (1g) (Tokuriki Honten Co., Ltd., Tokyo), and 50g of acrylic resin adhesive (Bond FL200, Konishi Co., Ltd., Osaka) were suspended in 1liter of water glass (SiO₂ 28-30%, Na₂O 9-10%, viscosity 100-250cp) (No.3, Fuji Kagaku Co, Osaka). This suspension was mixed with ceramic support (1kg) and then dried.

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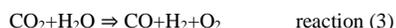
All the powders adhered to the surface of ceramic support with acrylic adhesive. The 6kg of this photocatalyst was set in the column. In this process, oxygen gas is converted to ozone, and further to reactive oxygen species such as superoxide anion radicals and hydroxyl radicals [4]. The reactive oxygen species may reduce carbon dioxide to carbon monoxide, as follows,



By using TiO_2 photocatalyst, H_2O was decomposed into H_2 and O_2 as follows,



As a total,



The activated water (10L) containing reactive oxygen species was mixed vigorously with either kerosene or light oil (10L) and carbon dioxide (from ambient air) to form an emulsion by the special mixer (Takemoto Industry, Okayama, Japan).

Analytical method

Alkane was analyzed by column chromatography with SHIMAZU GC-2010. The experimental conditions are shown below.

Vaporization room for specimen

Injection mode: split Total flow rate: 13.0 ml/min
 Temperature of vaporization room: 250°C
 Column flow rate: 1.81 ml/min
 Carrier gas: He Linear velocity: 40.0 cm/sec
 Control mode: linear velocity
 Purge flow rate: 4.0 ml/min
 Pressure: 142.0 kPa Split ratio: 4.0

Column oven: Column oven temperature program: initial 75°C,
 Rate: 6°C/min, Final 300°C, Hold 20 min
 Column: DB-1 (0.25µm × 30m) (J and W Scientific, California)

Detector

Detector: FID, Make up flow rate: 30.0 ml/min
 Detector temperature: 300°C, Flow rate of H_2 : 47.0 ml/min
 Make up gas: He, Air flow rate: 400.0 ml/min
 The inorganic impurities from commercial light were analyzed by X-ray Fluorescence.

Results and Discussion

Chemical Synthesis of Oil

Ten liter of light oil and activated water (10 liter) were collided against the wall of the mixer. The white emulsion (Figure 1) was left static until it separated into a two-phase (oil-water) solution (Figure 2). The volume of the oil fraction increased from the original volume by 5 to 10% and water fraction decreased by 5 to 10%. All reactions were carried out at room temperature and normal pressure.



Figure 1: White emulsion.



Figure 2: Oil production.

The oil generation reaction may occur as radical polymerization in emulsion and be written as follows,



This reaction is a part of Fischer-Tropsch process [5-7]. Generally, the Fischer-Tropsch process is operated in the temperature range of 150-300°C. Typical pressures range from one to several tens of atmospheres. Converting a mixture of H_2 and CO into aliphatic products obviously should be a multi-step reaction with several sorts of intermediates, 1) associative adsorption of CO , 2) splitting of the C/O -bond, 3) dissociative adsorption of 2H_2 , 4) transfer of 2H to the oxygen to yield H_2O , 5) desorption of H_2O , 6) transfer of 2H to the carbon to yield CH_2 . These processes are repeated as radical polymerization for the growth of the hydrocarbon chain. Why such intermediates are not detected in the present reaction will require further in-depth analysis. From reactions 3 and 4, mass balance is shown as follows,



Comparison between original light oil and new oil: The original oil and new oil (a mixture of original oil and newly synthesized oil) were analyzed by chromatography. SHIMAZU GC-2010 was used for the chromatographic analyses. Distribution of carbon number of original light oil was compared with that of new oil (Figure 3). Difference in compositional ratio at each carbon number was compared in Figure 4. Hydrocarbons with 15 (C_{15}) to 23 (C_{23}) carbon atoms increased in the new oil, whereas C_8 (or less) through C_{14} decreased and C_{24} through C_{27} (or more) decreased. These data clearly show that C_{15} through C_{23} was synthesized more efficiently than the original light oil and the lower number and higher number hydrocarbon were synthesized less. If all the fractions (C_8 through C_{27}) were synthesized at the same ratio, the difference of new oil and original oil should be zero. Thus we can conclude the chemical synthesis of hydrocarbon from CO_2 and water.

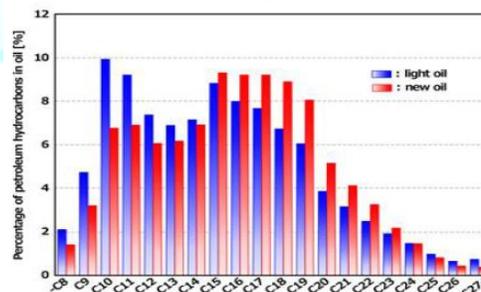


Figure 3: Comparison of composition between original light oil and new oil.

Characteristics of newly generated oil and the original oil are compared as shown in Table 1. No apparent difference between the two oil samples was recognized. A slightly higher value of gross heat generation in new oil may reflect the different distribution of carbon number.

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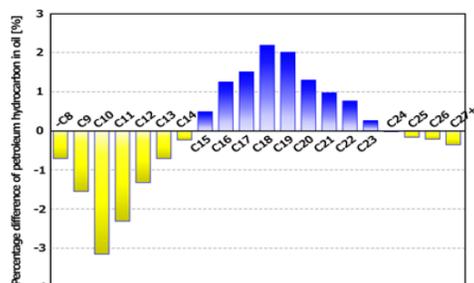


Figure 4: Difference in compositional ratio at each carbon number between original oil and new oil.

Item	Unit	Results		Method
		Original oil	New oil	
Reaction	-	Neutrality	Neutrality	JIS K2252
Flash point (PMCC)	°C	73	74	JIS K2265-3
Viscosity (30°C)	mm ² /s	3.479	3.479	JIS K2283
Fluidity point	°C	-15	-12.5	JIS K2269
Residual carbon	Mass%	0.01	0.01	JIS K2270-2
Water, KF method	Mass%	0.0063	0.0049	JIS K2275
Ash	Mass%	0.001	0.001	JIS K2272
Sulfur	Mass%	0.0007	0.0007	JIS K2541-6
Density (15°C)	g/cm ³	0.8295	0.8297	JIS K2249-1
Distillation temp.				JIS K2254
10% distillation	°C	217	226	
50% distillation	°C	271.5	274.5	
90% distillation	°C	326	329.5	
Cetane number	-	56.2	56.5	JIS K2280-5
Gross heat generation	J/g	45,990	46,010	JIS K2279
Choked point		-10	-12	JIS K2269

Note: JIS-Japanese Industrial Standards.

Table 1: Characteristics of original and new oils.

Production of Specific Carbon Number n-Alkane

In order to examine the possibility of producing oil with a specific carbon number, the special grade of tetradecane (C₁₄) was purchased from Wako Pure Chemicals (Osaka, Japan) and used as the original oil for this reaction. The volume of new tetradecane increased by 7%. The chromatographic data are shown in Figure 5a, Figure 5b and Figure 5c. Figure 5a shows the chromatogram of hexane (C₆) used as the solvent. Figure 5b shows the chromatogram of the original tetradecane.

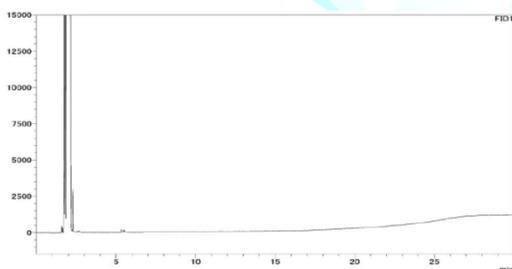


Figure 5a: Chromatogram of hexane as solvent.

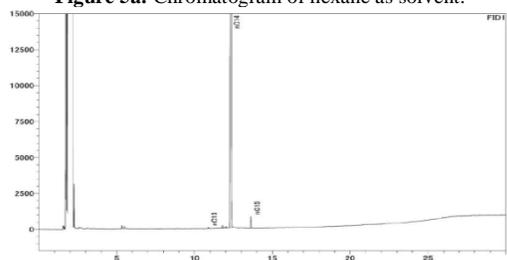


Figure 5b: Chromatogram of original tetradecane.

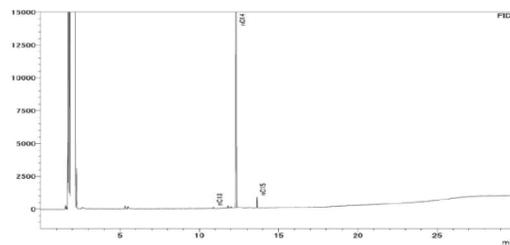


Figure 5c: Chromatogram of newly synthesized material from tetradecane.

The original sample of tetradecane is composed of 0.021% tridecane (C₁₃), 99.804% C₁₄, and 0.175% pentadecane (C₁₅). The new oil contained 0.023% C₁₃, 99.793% C₁₄, and 0.184% C₁₅. Although the oil volume increased, no apparent difference of chromatographic data was observed. Original tetradecane may be used as a template for the synthesis of new tetradecane. These data show that specific carbon number hydrocarbon (alkane) could be synthesized depending on the original alkane. Therefore it is easily understood that light oil was produced with light oil and kerosene was synthesized with kerosene.

Purification of Commercial Light Oil

Commercial light oil was purchased from gasoline stand, and treated likewise. The volume of oil was increased by 5-10% as mentioned above. Surprisingly after the reaction, organic soot fraction (impurity from commercial light oil) appeared in the water fraction at oil-water interface (Figure 6). At the same time, inorganic impurities appeared at the bottom (Figure 7). The inorganic impurities include mainly Fe, Si, Zn, and a little amount of K, S etc.



Figure 6: Soot fraction from commercial light oil.



Figure 7: Inorganic impurities from commercial light oil.

Color of commercial light oil and newly synthesized oil was compared (Figure 8). Commercial light oil (left) showed dark yellow and new oil (right) showed pale yellow, because organic and inorganic impurities were removed from commercial light oil. When this clean new oil was repeatedly used for the next process, new clean oil was produced, indicating inexhaustible synthesis.



Figure 8: Comparison of commercial light oil (left) and new oil (right).

Application of New Oil

Since newly synthesized clean light oil meets strict Japanese Industrial Standards (Table 1), the performance was examined by using diesel engine. In fact, one 10 ton truck, two 4 ton trucks, and a sedan car were used. The results were very good. (1) Traveling distance was extended by 1.15 ~ 1.50 fold. (2) Exhaust gas became clear. Amount of soot decreased drastically. (3) Knocking was hardly experienced, indicating anti-knocking. (4) Engine sound was getting more quiet. Since the clean light oil is excellent, it was named as “Dream Light Oil”.

Conclusion

Petroleum (light oil, kerosene, n-alkane) could be formed efficiently at normal temperatures and pressures from carbon dioxide and activated water. The CO₂ nano-bubble containing water was treated with photocatalyst in the presence of oxygen under UV irradiation. The activated water was mixed vigorously with kerosene or light oil to form an emulsion. The emulsion gradually separated into a two-phase solution. After phase separation, the volume of kerosene or light oil, depending on which oil was utilized, increased by 5 to 10%. Likewise, tetradecane was used as a template in the experiment, only tetradecane was newly synthesized. When commercial light oil was treated in the same way, most organic and inorganic impurities were removed from oil and very clean light oil was obtained. We named it as dream light oil. The dream light oil meets strict Japanese Industrial Standards. The oil showed very excellent performance for diesel engine.

Since this oil production process is cheap and effective, this technique is extremely important to deal with the current energy crisis, and should provide a foundation for carbon-neutral energy production. The method simultaneously utilizes/reduces carbon dioxide (greenhouse gas) as it is consumed as a carbon source when converted to hydrocarbons. Since the newly synthesized oil does not contain sulfur, SO_x is not exhausted from the combustion gas. This result may also support the abiotic petroleum origin hypothesis.

These results can be summarized as follows; (1) Fuel hydrocarbon can be synthesized efficiently at normal temperatures and pressures from carbon dioxide and activated water. (Inexhaustible resources), (2) Gross heat generation of original oil and new oil were the same, (3) High productivity, (4) High cost performance (Efficient process), (5) Oil is used as a template for next oil synthesis, (6) No need to purify the new oil, because S and N are not contained in the dream oil. Thus, SO_x and NO_x are not generated after burning (Earth friendly), (7) Soot fraction and other impurities were removed from commercial light oil, and the new dream oil showed excellent performance for diesel engine, (8) Since CO₂ in the air is mainly consumed, this process contributes to global warming prevention. (Emissions trading is advantageous), (9) Carbon neutral, (10) Abiotic synthesis of petroleum, (11) Energy crisis will be avoided.

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