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Process Simulation of Diesel into Aromatics and Carbon Nanotubes: A Techno and Economic Analyses

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ABSTRACT: With the sustainable increase of renewable energy and the maturation of heavy vehicle market, diesel consumption would face a downward trend worldwide. Herein, we have proposed a new route for hydrocracking of light cycle oil (LCO) into aromatics and gasoline and the tandem conversion of C_1–C_5 hydrocarbons (byproducts) into carbon nanotubes (CNTs) and H_2, and by combining the simulation with Aspen Plus software and the experimental study of C_2–C_5 conversion, we have built a transformation network including LCO to aromatics/gasoline, C_2–C_5 to CNTs and H_2, the conversion of CH_4 into CNTs and H_2, and the cycle use of H_2 with pressure swing adsorption. Mass balance, energy consumption, and economic analysis were discussed as a function of varying CNT yield and CH_4 conversion. 50% of H_2 required for hydrocracking of LCO can be supplied by the downstream chemical vapor deposition processes. This can greatly reduce the cost of high-priced hydrogen feedstock. If the sale price of CNTs exceeds 2170 CNY per ton, the entire process would break even for a process of dealing with 520,000 t/a LCO. These results imply the great potential of this route, considering the vast demand and the current high price of CNTs.
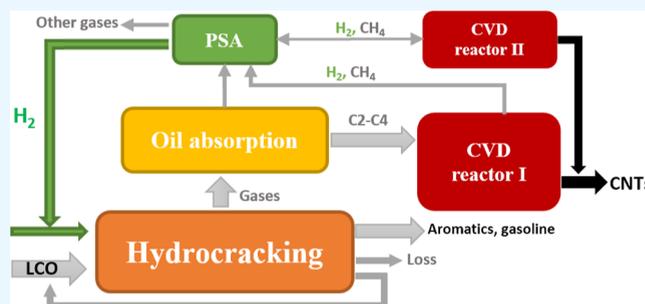
1. INTRODUCTION

With the sustainable increase of renewable energy, the consumption of diesel is approaching the highest level and facing a declining usage trend. Such a condition calls for the further transformation of diesel into high-end chemicals and high-end materials. Hydrocracking of light cycle oil (LCO), a type of diesel, is effective in producing aromatics and gasoline,[1-6] but it is consumed in H_2 production. In addition, the large amount of C_1–C_5 paraffin byproducts also affects the economy of the process. On the other hand, the chemical vapor deposition (CVD) method is mature enough to convert hydrocarbons, including methane[7-9], olefins, LPG,[10,11] etc., into carbon nanotubes (CNTs).[12-15] CNTs are a type of high-end nanomaterials and are finding wide applications as additives to Li-ion batteries,[16,17] catalyst supports,[18] electrode materials of supercapacitors,[19,20] and reinforced and conductive components in composites made of polymers, metals, and ceramics.[21-23] However, most of the studies have focused on the quality control of CNTs but not yet on the production of hydrogen.[7,10,12,13] (see Table 1)

In the present work,[24] we have proposed a new approach that combines upstream hydrocracking of LCO with downstream transformation of C_1–C_5 hydrocarbons into CNTs and H_2 to maximize H_2 production and reuse downstream H_2 for LCO hydrocracking. Considering that though data of the upstream procedure were sufficient, some data of the

Table 1. Conversion of CH_4 to CNTs under Different Catalysts and Different Temperatures

catalyst	reaction temperature/K	CH_4 conversion rate	CNT yield	refs
Ni/Cu/Al$_2$O$_3$	1123	40%	no data	9
iron-based catalyst	873	80%	no data	25
FeCl$_3$	1323.15	no data	80%	28
iron oxide-MgO	1223.15	no data	30%	29

downstream procedure were lacking, a combination of process simulation with a heat model CVD experiment was carried out in the present work. The decomposition of light hydrocarbons (C_2H_6, C_2H_4, LPG, C_5H_{12}, and C_5H_{10}) to CNTs was experimentally explored, in which products were controlled to be mainly H_2 and CH_4. We have discussed the mass balance, energy consumption, and economic feasibility of the total route, as a function of varying the CNT yield and the conversion of CH_4. Based on the normal sale price of LCO,
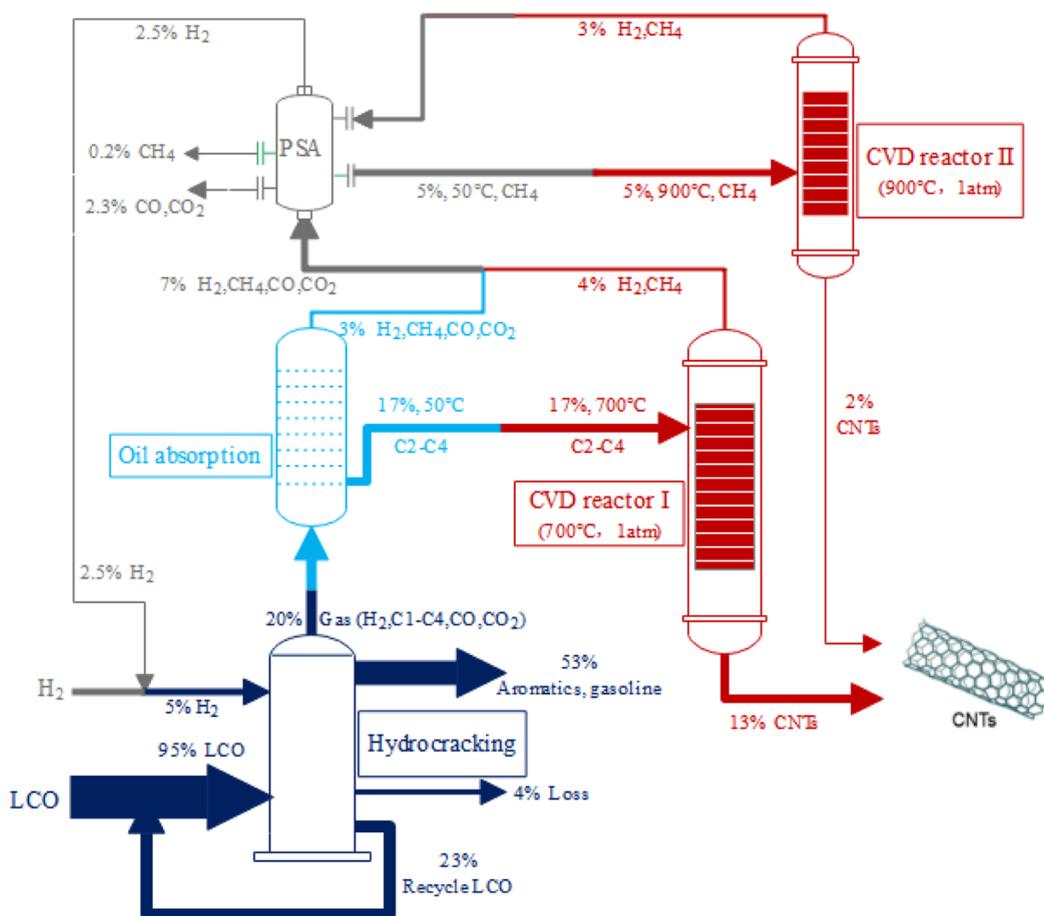
Figure 1. Overall flow chart.

H_2, aromatics, and gasoline, we were able to evaluate the effect of sale price of CNTs on the economic aspects of the entire process. The present work has proposed an effective route for upgrading LCO in a huge amount to high-end products with economical interest.

2. RESULTS AND DISCUSSION

2.1. Technical Route from Diesel to Aromatics/Gasoline and CNTs. Overall, we need to create a product flow chart that uses LCO to produce aromatics and gasoline and further converts light hydrocarbon byproducts into CNTs, integrating necessary separation units step by step. The overall flow rate is qualitatively described in Figure 1. Of course, the mass flow data should be quantitatively determined by the experiments and process simulation as follows.

In industry, there was a technology called LCO to aromatics and gasoline (LTAG) by hydrocracking. Such a unit was directly adopted in the present work. Generally, LCO enters the hydrocracking unit and is converted with the catalyst at 500−600 °C and high pressure into the main products of high-octane gasoline and aromatic hydrocarbons. Byproducts included dry gas (H_2, CH_4, CO, and CO_2), LPG (C_2−C_4 light hydrocarbons), untransformed LCO, and some heavy slurry (which was used for burning to provide energy). Since the conversion of LCO was difficult, approximately 23 wt % of untransformed LCO was recycled into the hydrocracking unit (Figure 1). 53 wt % of gasoline and aromatic products were sold through subsequent separation processes. Thus, 20 wt %

of gaseous hydrocarbons needed to be further converted, which was the focus of the present work.

In general, as also shown in Figure 1, gaseous hydrocarbon products could be further separated in the oil absorption system, a downstream post-processing system of hydrocracking. Such a separation unit was also mature in industry and directly adopted in the present work. According to the data of Yan et al.,[32] the temperature at the top of the oil absorption tower was about 50 °C, so the outlet temperature of dry gas and LPG was assumed to be 50 °C. For the further conversion of LPG into CNTs and H_2 in CVD reactor I, the operating conditions were set to be 700 °C and 1 atm. Mostly carbon elements of LPG were fixed as CNTs. The amounts of gaseous products (H_2 and CH_4) were determined experimentally in the present work. As follows, separation of H_2 and CH_4 by the PSA unit was a mature technology, as well as a small amount of CO and CO_2 was produced throughout the process. Most of the CH_4 isolated from PSA was transferred into CVD Reactor II for further reaction, and H_2 and CNTs were obtained as the products. The reaction temperature of CVD Reactor II was higher than that of reactor I, which was set as 900 °C. H_2 and CH_4 from CVD reactor II continue to enter PSA, and the H_2 separated from PSA completely circulated back to the hydrocracking unit.

The process of producing CNTs and H2 from light hydrocarbons was simulated using Aspen Plus V11 software, and the energy consumption of the reaction was calculated. The remaining energy consumption estimation was obtained from relevant literature.[31]
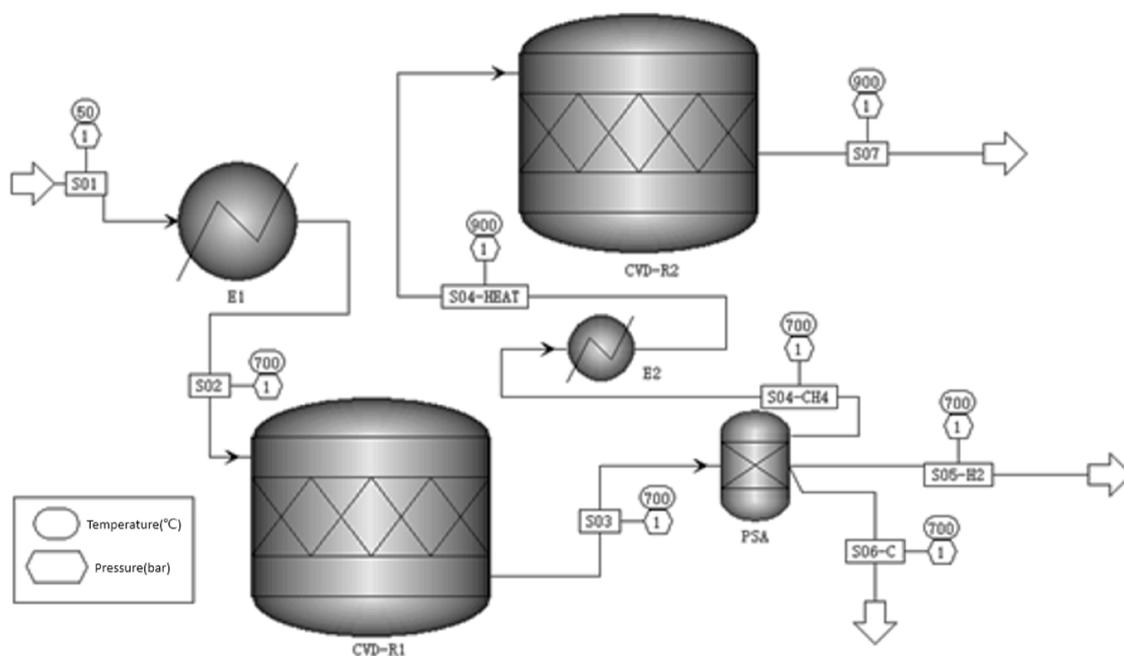
Figure 2. Flow chart of Aspen Plus modeling of CNTs and H_2 from light hydrocarbons.

As also shown in Figure 2, the RSTOIC module (stoichiometric reactor) of Aspen Plus software was utilized to simulate the reaction process of methane, ethylene, ethane, propylene, propane, butene, and butane for producing CNTs and H_2 at 700/900 °C and 1 atm. The feed temperature was determined based on the outlet temperature at the top of the stabilized tower in the absorption stabilization system in the previous step. The inlet temperature of the heater was 50 °C, and the outlet temperature was set to 700 °C for CVD reactor I and 900 °C for CVD reactor II. In addition, an SEP module (component separator) PSA was used to separate H_2, methane, and CNTs. The SEP module can separate various substances according to the setting, without considering the separation energy consumption. The subsequent separation energy consumption can be estimated through actual industrial production. The physical property method of this model was PENG-ROB, which was often used in gas processing simulation, such as light hydrocarbon separation. Two tables containing the modeling information from Aspen Plus are presented in Supporting Information S3, The modeling information from Aspen Plus.

2.2. Experimental Data for Converting Light Hydrocarbons into CNTs. The experiments proved that CNTs and H_2 were prepared from C2+ light hydrocarbons at a reaction temperature of 700~800 °C, and the main products were CNTs, H_2, and methane Figure 3.

The experimental conditions are as follows: ① A quartz-made fluidized-bed reactor with an inner diameter of 50 mm and a height of 2 m was used as the CVD reactor for the conversion of hydrocarbon feedstock. Nitrogen (15 mL/s) was used as the carried gas, and all catalyst powder (Fe/Mo/Al$_2$O$_3$, 30−70 μm, packing density of 750 kg/m^3) was suspended by gases. As the CNT was produced, the packing density of solids become more and more small until 200 kg/m^3. Thus, all solids are suspended in a gas velocity range of 0.05−0.1 m/s. ② Gas products flowing out of the exit of the reactor were in-situ-analyzed with gas chromatography (Agilent-7890D) equipped with one TCD column and two FID detectors. ③ For the
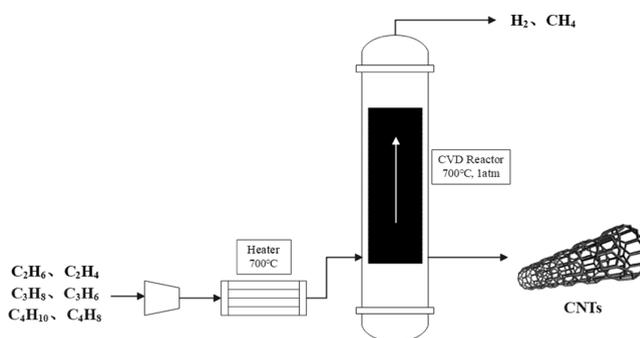
Figure 3. Flow chart of preparation of CNTs from light hydrocarbons.

conversion of each kind of hydrocarbon, experiments were done 5 times, the average value of the CNT yield was determined, and the obtained conversion rate was used in the paper.

According to the experimental data, the feed gas conversion rate and carbon yield of CNTs prepared by ethane, ethylene, LPG, pentane, and pentene were determined, as shown in Figure 4. The yield of CNTs was the ratio of the mass of produced CNTs to the mass of carbon in the feed gas. From Figure 4, we can see that the conversion rate was between 97 and 100%, and the CNT yields were between 60 and 80%. The method of CNT collection can be optimized to avoid collection error according to the actual industrial situation, and the yield of CNTs can be further increased.

In addition, a large amount of methane was generated during the conversion of C_2-C_5 hydrocarbons in CVD reactor I. So, methane should be further added to CVD reactor II for reaction to obtain CNTs and H_2. It was used to discuss mass balance of the entire transformation network of LCO. From most of the references on the preparation of CNTs from methane, the conversion rate of methane varies greatly and was both temperature- and catalyst-dependent.[8,9,25−29] Considering the industrial practicability, a temperature of 900 °C and the
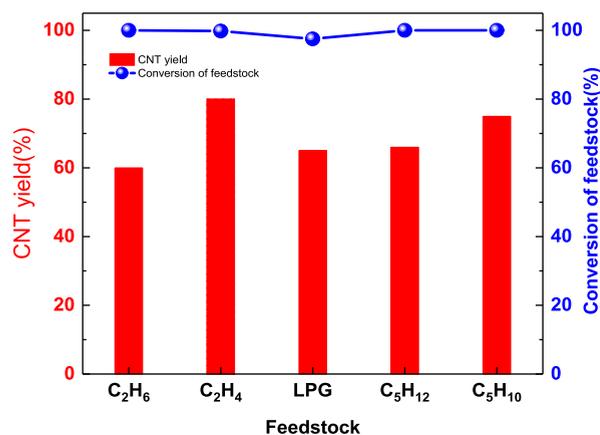
Figure 4. CNT yield and conversion rate of C_2H_6, C_2H_4, LPG, C_5H_{12}, and C_5H_{10} converted to CNTs.

Figure 5. Product distribution under different CNT yields and CH_4 conversion rates.

actual conversion rate of methane in the range of 30−50% were adopted here for process simulation.

In detail, we considered the CNT yields in the range of 60−90% and CH_4 conversion rates in the range of 30−50%. Thus, the associated cycle flow and energy consumption in separation can be obtained for the analysis of the overall economic value in all cases. The chemical equations for the conversion of light hydrocarbons to CNTs and H_2 are shown in Supporting Information S2, CNTs and H_2 from light hydrocarbons. Figure 1 shows a case of quantitative mass flow network. 20% gaseous products contributed 15% CNTs in total, 2.5% H_2 in total, 0.2% CH_4, and 2.3% CO/CO_2 (hydrocracking feedstock base). H_2 was used for hydro-cracking. This would be ideal and simple if part of CO/CO_2 entering the CVD reactor to make CNTs or produce H_2O to consume H_2 is not considered. However, the error by a small portion of CO/CO_2 in CVD would be small and negligible for the evaluation of the entire process.

Overall, the gross mass flow can be balanced as feeding 5 wt % H_2 and 95 wt % LCO into the hydrocracking unit (Figure 1). Thus, 50% H_2 should be supplied from the outside, while 50% can be supplied from the downstream CVD unit.

2.3. Analysis on the Whole Technical Route.
2.3.1. Distribution of Products under Different Carbon Yields. The LTAG technology developed by Sinopec Research Institute of Petroleum and Chemical Engineering was adopted in this study, and the industrial application data of LTAG technology published by Yan et al.[30] were used to conduct simulation calculation and discussion. Refer to Supporting Information S1, Product composition of LTAG and flow chart, for details of the product distribution of LTAG.

According to the above, after hydrocracking, oil adsorption, PSA, and CVD reaction of LCO and H_2, we can obtain CNTs, H_2, CH_4, CO, CO_2, and gasoline/aromatics, recycle LCO, and determine the loss (retarded and burned). Figure 5 shows the distribution of the products without considering the recycling of H_2. The amounts of CNTs, H_2, and CH_4 varied under different CNT yields, while the amounts of CO, CO_2, gasoline, recycle LCO, loss (slurry and burned) were all the same. As the carbon yield increased, the content of CNTs and H_2 increased, while the content of CH_4 decreased. Actually, the high selective conversion of LPG contributed to the H_2 production with high efficiency (Figure 4), considering CH_4 was much tough to convert. CH_4 could be considered as the
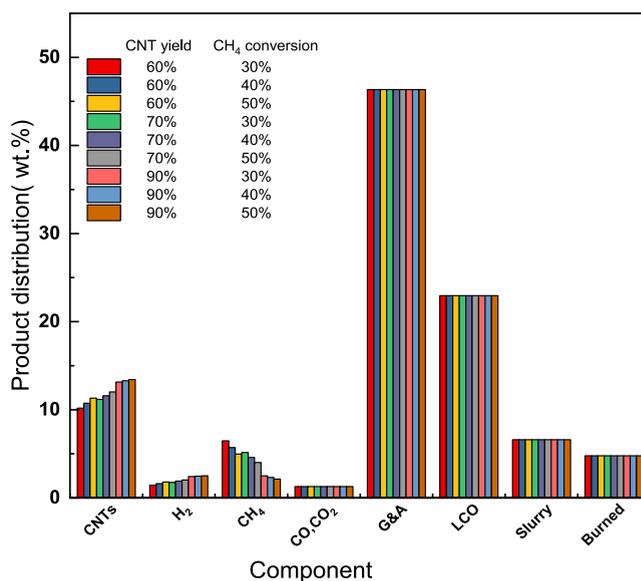
competitive component in the transformation of LPG into CNTs and H_2.

2.3.2. Economical Analysis. Supporting Information S4, Material input and output price calculation, lists the detailed calculation process and the prices of input and output materials, annual output, energy cost per unit, and annual profit. The prices of LCO, H_2, CH_4, gasoline, aromatics, and recycled LCO were referenced to the market average price and the prices in relevant literature. The energy cost of LTAG was calculated by industrial data in the literature.[31] The energy cost of preparing CNTs and H_2 from hydrocarbons was calculated by simulation using Aspen Plus.

The annual output of all products was calculated based on the product distribution and the annual processing capacity of LCO (520,000 tons). The annual profit was calculated by the annual output and price of products, as well as the energy consumption cost of each unit. Since CNTs were sold at different prices depending on their uses, the annual profit calculated in Supporting Information S4, Material input and output price calculation, did not include revenue from the sale of CNTs.

Figure 6a shows the trend of the price of CNTs on the overall profit under different carbon yields. It was clear that when the price of CNTs was fixed, the higher the yield of CNTs, the higher the CH_4 conversion rate and the lower the overall profit. Actually, the conversion of $C_1−C_4$ paraffins into CNTs and H_2 was endothermic. Higher conversion of the feedstock needed a higher energy input. In detail, the conversion of LPG was less endothermic reaction, as compared to the conversion of CH_4 (into CNTs and H_2). When the two variables increased, the corresponding reactor energy con-sumption and separation energy consumption between H_2 and CH_4 in PSA would also increase, leading to a decline in the overall profit. In addition, the higher the yield of CNTs, the higher the CH_4 conversion rate, and the slope of the curve in the figure was larger, indicating that the price of CNTs has a greater impact on the overall profit.

Figure 6b shows the change in the break-even point under different CNT yields and CH_4 conversion rates. With the increase of CNT yield, the CH_4 conversion rate increased and
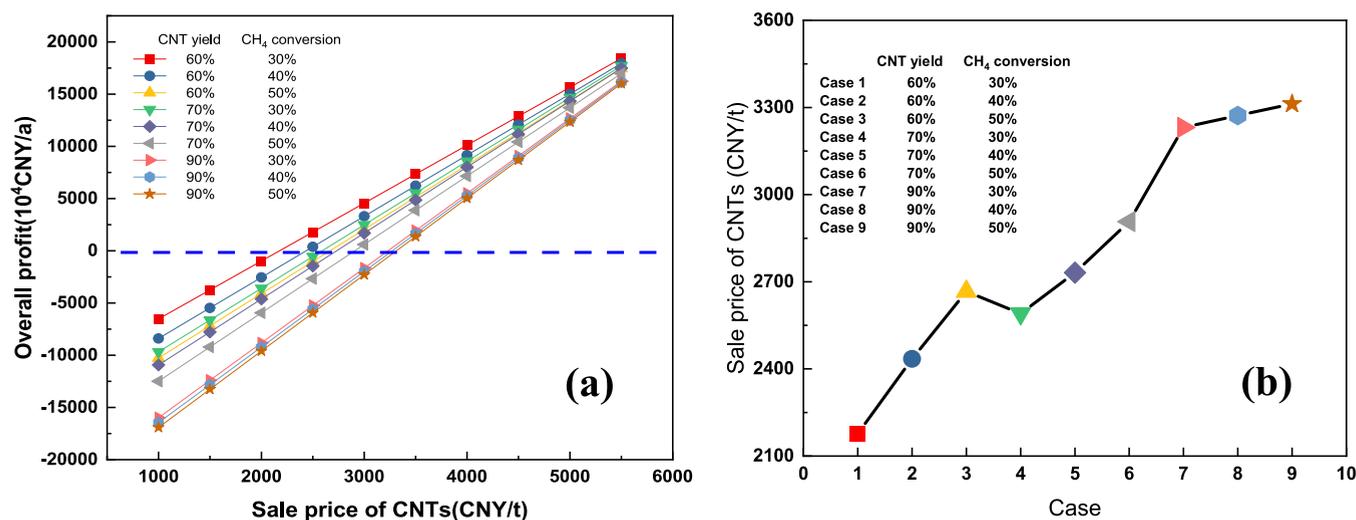
Figure 6. (a)Effect of CNT price on profit under different CNT yields and CH_4 conversion rates. (b) Break-even points under different CNT yields and CH_4 conversion rates.

the break-even point increased. Apparently, for these endothermic processes of LPG or CH_4 to CNTs and H_2, the increased CNT yield and the increased conversion of CH_4 were at the expense of increased heat supply. Thus, sale price of CNTs should be increased to offset the cost of energy. Quantitatively, when the CNT yield was 60% and CH_4 conversion rate was 30%, the production of CNTs was 55450.65 tons/year. The sale price of CNTs to make the process break even was 2176.75 CNY/ton. Similarly, when the CNT yield was 70% and CH_4 conversion rate was 40%, the production of CNTs increased to 63152.13 tons/year. Thus, the sale price of CNTs should be increased to 2754.63 CNY/ton accordingly to make the process break even. For an extreme case of very high CNT yield (90%) and a high CH_4 conversion rate (50%), the production of CNTs would be 73164.05 t/a and the sale price of CNTs should be 3312.36 CNY/ton to make the process break even. From the calculation above, it was clear that the high energy consumption in the CVD process and separation unit was a key factor to influence the sale price of CNTs. The sale price of CNTs would fluctuate nearly 30−50% accordingly.

According to the current market demand, the product form of CNTs was mainly divided into powder and paste, and the market demand ratio of powder was about 4.5%.[33] Current supply of CNT powder was mainly multi-walled CNTs (MWCNTs), with a price of $100/kg[34] for industries of high-voltage cables, integrated circuit packaging, semiconductors, and electromagnetic shielding materials.[33] Currently CNT paste (5% CNTs and 95% *N*-methyl pyrrolidone) constitutes a huge market for batteries, with a fluctuating market price between 40 and 70 CNY/kg.[35] Anyway, these sale prices of CNTs were too high compared to our evaluation prices (2200−3300 CNY/t, which were 2.2−3.3 CNY/kg) of CNTs in mass production (Figure 6b). This implied that the CNTs produced in the LCO transformation network easily found application in current market, considering these huge price advantages.

In the following, the relationship between the CNT price and their yield was evaluated. Figure 7 shows the impact of CNT price on the output under different CNT yields and CH_4 conversion rates when the break-even point was reached. In detail, for a very limited yield of CNTs (402 t/a), the sale price
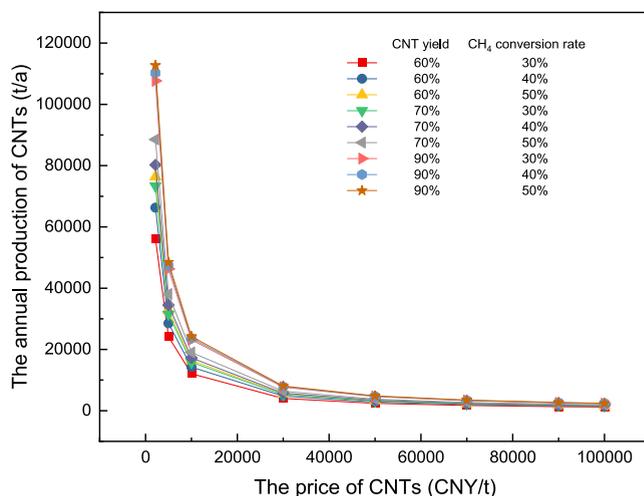
Figure 7. Effect of CNT price on production under different CNT yields and CH_4 conversion rates when the break-even point was reached.

of CNTs should be high up to 300,000 CNY/ton to achieve break even. With the drastic increase of the CNT yield, the prices of CNTs will drop accordingly. It was 100,000 CNY/ton for a yield of 1207 t/a and 10,000 CNY/ton for a yield of 12,070 t/a.

Therefore, the technological process proposed in this paper is very affordable. It is quiet favorable for the scale-up of the CNT production. In addition, LCO generates 2.5 wt % H_2 for hydrocracking as mentioned above. This will significantly alleviate the burden of H_2 supply for hydrocracking. Note that, in this simulation calculation, the actual separation cost of selling pure hydrogen from PSA was used. Since about half of the hydrogen here can be recycled back to the hydrocracking process, the required H_2 purity was not so high. Thus, a large part of the separation cost can be reduced and the sale price of CNTs can be further decreased for the purpose of break even. These features will make the process more sustainable.

3. CONCLUSIONS

We proposed the technology route of transforming LCO into aromatics and gasoline and further converting the gaseous hydrocarbons into CNTs and H_2 by two steps including C_2−C_5 conversion and CH_4 conversion. Finally, all collected H_2 was recycled for hydrocracking. It was concluded that CNT yield and CH_4 conversion were indeed two key factors influencing the energy consumption and break-even point of the entire process. Increased CNT yield and increased CH_4 conversion both increased energy consumption, and the sale price of CNTs should be increased accordingly to make break even. For the process of dealing with LCO with a capacity of 520,000 t/a, the cost of CNTs was higher than 2170 CNY per ton, and the entire process will break even, assuming the separation cost of pure H_2 in PSA was 0.7 CNY/m³. It was very easily realized considering its current sale price which exceeded 100,000−150,000 CNY per ton. The dependent relationship between CNT yield and CNT prices was calculated. Increased CNT will offset the energy consumption of the process, allowing a decreased sale price of CNTs. The present simulation suggested a typically low sale price of CNTs from the LCO transforming network. The CNT product, if sold at the current market price, would provide a huge advantage in competition to meet various application requirements.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c01135.

Product composition of LTAG and flow chart, CNTs and H_2 from light hydrocarbons, modeling information from Aspen Plus, material input and output price calculation, and energy consumption of light hydrocarbon to CNTs and hydrogen (PDF)

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Notes
The authors declare no competing financial interest.

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