



Low- H_2 Used Cooking Oil Deoxygenation over a Multifunctional Catalyst: Product-Window Redistribution under H_2 /Formic Acid Assistance

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Abstract

The catalytic conversion of used cooking oil (UCO) to green diesel is not only a conversion problem but also a pathway-control and product-window optimization problem. UCO-derived triglycerides and fatty acids can undergo hydrodeoxygenation (HDO), decarbonylation (DCO), decarboxylation (DCO_2), cracking, and secondary redistribution reactions. In this study, a multifunctional $Ni-MgO-Ce_{0.6}Zr_{0.4}O_2/\gamma-Al_2O_3$ catalyst was applied for UCO deoxygenation under four hydrogen-supply modes: Catalyst (C), $C+H_2$, $C+FA$ (formic acid), and combined $C+H_2+FA$ operation. The reactions were compared at 320°C and 350°C, and the products were analyzed by GC-TCD, GC-FID, and DGC/SimDist. The 320°C condition served as a lower-severity reference, where diesel-range products were generally better preserved, whereas 350°C promoted stronger liquid-phase upgrading, higher distillable-product formation, and more effective residue suppression. At 350°C, the distillable fraction below 370°C increased from 78.3% in the catalyst (C) mode to 98.6% in the $C+H_2+FA$ mode, while residue decreased from 21.7% to 1.4%. However, this improvement was accompanied by product lightening, with the diesel-range fraction decreasing from 42.3% to 22.4% and the naphtha-range fraction increasing from 23.8% to 56.8%. Gas analysis showed CO -rich products in the catalyst (C) mode, supporting a strong DCO tendency even without external H_2 , while FA -containing modes increased CO_x formation due to both UCO deoxygenation and possible FA decomposition. In the closed reactor, FA -derived gas formation may also have increased internal pressure and contributed to higher reaction severity and product lightening. Overall, the catalyst shows promise for controlled low- H_2 deoxygenation, but secondary cracking and excessive light-product formation must be controlled.

Keywords : used cooking oil; multifunctional catalyst; deoxygenation; formic acid; low H_2

Introduction

Green diesel is an important renewable hydrocarbon fuel because its properties are closer to petroleum diesel than conventional fatty acid methyl ester biodiesel. It contains negligible oxygen and is mainly composed of paraffinic hydrocarbons, giving improved oxidative stability, higher cetane quality, and good compatibility with existing diesel engines and fuel infrastructure [1-3]. Used cooking oil (UCO) is a promising lipid-based feedstock because it is inexpensive, widely available as a waste resource, and can reduce both environmental burdens and competition with edible oils [4, 5]. Therefore, converting UCO into diesel-range hydrocarbons is a relevant pathway for circular renewable fuel production.

Catalytic deoxygenation of UCO mainly proceeds through hydrodeoxygenation (HDO), decarboxylation (DCO_2), and decarbonylation (DCO) [1, 3, 6]. These pathways differ in hydrogen demand and carbon efficiency. HDO removes oxygen mainly as H_2O and generally preserves the original fatty-acid carbon number, whereas DCO_2 and DCO remove oxygen as CO_2 and CO and usually shorten the hydrocarbon chain by one carbon atom [6, 7]. Although HDO can retain more carbon in the liquid product, it requires substantial external H_2 , commonly under elevated pressure. In contrast, DCO_2 /DCO can reduce direct H_2 consumption but may lower liquid carbon recovery. Thus, low- H_2 green diesel production requires pathway control rather than simple conversion maximization.

The dependence on external H_2 remains a major technical and economic limitation of green diesel production because high-pressure H_2 increases process complexity, equipment cost, and safety requirements [1, 4, 5]. For this reason, recent studies have explored H_2 -lean, H_2 -free, and donor-assisted systems as alternatives to fully hydrogen-rich operation [8-10]. H_2 -free deoxygenation over Ni/MgO- Al_2O_3 has shown that green diesel-like hydrocarbons can be produced from fatty-acid model compounds without direct gaseous H_2 , although pathway selectivity and carbon loss remain key challenges [9, 10]. Other Ni-based H_2 -free systems have also been proposed

for biomass upgrading through in situ hydrogen generation or transfer-hydrogenation-related mechanisms [11].

Nickel-based catalysts are attractive for reduced- H_2 deoxygenation because Ni is cheaper than noble metals and can promote hydrogenation, C–O bond cleavage, and deoxygenation reactions [8, 9, 12]. However, Ni may also promote cracking, methanation, coke formation, or excessive DCO/ DCO_2 [8, 12]. Accordingly, the present catalyst was designed by combining several complementary catalytic functions reported in previous studies. MgO was incorporated to introduce basic sites, which have been enhanced decarboxylation-related activity and moderation of the acidic character of alumina [9, 10]. CeO_2 – ZrO_2 -based oxides were selected because of their redox properties, oxygen-storage/transport capability [15, 16]. γ - Al_2O_3 was used as a high-surface-area structural support to disperse the active phases and provide mechanical stability. By integrating metallic Ni, basic MgO, redox-active $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$, and γ - Al_2O_3 within a single catalyst, therefore the Ni–MgO– $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ / γ - Al_2O_3 formulation was selected as a multifunctional system for investigating pathway control under reduced- H_2 UCO deoxygenation.

In addition to Ni/ Al_2O_3 -based systems, bimetallic Ni, Co-based, Ni–W, phosphide, and carbide catalysts have also been investigated for green diesel production. These studies demonstrate that catalyst composition strongly influences deoxygenation activity and the resulting diesel-, kerosene-, and gasoline-range product distribution [5, 12-14, 17, 18].

Hydrogen-donor-assisted operation is another strategy for reducing direct H_2 dependence. Alcohols, glycerol-derived compounds, water-assisted systems, and other hydrogen-transfer media have been investigated as possible sources of in situ hydrogen or hydrogen-transfer species [11]. Formic acid (FA) is an attractive hydrogen donor because it can serve as an in-situ hydrogen source while also generating CO and CO_2 , potentially reducing external H_2 demand and modifying the reaction environment during deoxygenation. However, donor-assisted operation complicates pathway interpretation because

donor decomposition may generate H_2 , CO , CO_2 , or oxygenated intermediates. Therefore, gas-phase CO and CO_2 should not be interpreted only as direct indicators of UCO-derived DCO/DCO₂, but should be considered together with liquid yield, carbon-number distribution, and boiling-range redistribution.

In this study, a multifunctional catalyst was applied for UCO deoxygenation under four hydrogen-supply modes, comparing reactions at 320°C and 350°C.

Materials and Methods

Catalyst Preparation

The experiments were carried out using a multifunctional $Ni-MgO-Ce_{0.6}Zr_{0.4}O_2/\gamma-Al_2O_3$ catalyst. The catalyst was synthesized by a sequential incipient wetness impregnation method. In the preparation sequence, the Ce–Zr oxide phase was first deposited on the $\gamma-Al_2O_3$ support, followed by MgO modification and subsequent Ni loading. Before use in the catalytic reaction, the catalyst was pre-reduced under flowing H_2 at 30 mL min⁻¹. The temperature was increased to 500°C [8] at a heating rate of 2°C min⁻¹ and maintained at this temperature for 2 h.

UCO Collection and Preparation

Used cooking oil (UCO) was employed as the renewable lipid feedstock. The UCO was collected from palm oil used for deep-frying Chinese fried dough sticks over a seven-day period, during which approximately half of the oil was periodically replaced with fresh oil. Prior to catalytic testing, the collected UCO was filtered to remove suspended particles and then heated at 60°C for 30 min to reduce residual moisture. The moisture content of the prepared UCO, determined by a gravimetric method, was 0.058 wt%. For each experiment, 6.0 g of UCO and 0.6 g of catalyst were loaded into a 70 mL cylindrical batch reactor fitted with a gas-tight cover. The catalyst amount corresponded to 10 wt% relative to the UCO feed. The reaction was conducted in an electrically heated reactor system equipped with oscillatory mixing at 1.6 cycles min⁻¹ (Figure 1). All experiments were performed at

320°C and 350°C with a holding time of 1 h after reaching the target temperature.

Experimental Conditions and Run

In this study, four hydrogen-supply modes (as defined in Table 1) were designed to compare the effect of hydrogen management on UCO deoxygenation. The first mode, Catalyst (C), contained neither external H_2 nor formic acid (FA). The C+ H_2 mode, employed the catalyst together with gaseous H_2 . The C+FA mode, employed the catalyst with FA as the hydrogen donor without external H_2 . The C+ H_2 +FA mode, combined the catalyst, external H_2 , and FA. For the C+ H_2 and C+ H_2 +FA modes, the reactor was initially charged with H_2 to 0.9 MPa. In the C+ H_2 mode, the hydrogen input was equivalent to 3 mol H_2 per mol UCO. In the C+FA mode, 2.2 g of FA was added, corresponding to 6 mol FA per mol UCO. In the C+ H_2 +FA mode, the reactor was charged with H_2 at 3 mol H_2 per mol UCO together with 1.1 g of FA, corresponding to 3 mol FA per mol UCO. This experimental design allowed direct comparison among C, C+ H_2 , C+FA, and C+ H_2 +FA modes under the same reaction temperature and residence time.

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Analytical Techniques

After reaction, the gas and liquid products were separately analyzed. The gas phase was analyzed directly by GC-TCD (Model Agilent technology, GC7820A), with emphasis on H_2 , CO , CO_2 , and other permanent gases. The liquid phase was characterized by GC-FID and simulated distillation (SimDist) (Model Agilent technology, GC7820A). GC-FID was used to evaluate the hydrocarbon carbon-number distribution of the liquid products, while SimDist was applied to determine the boiling-range distribution.

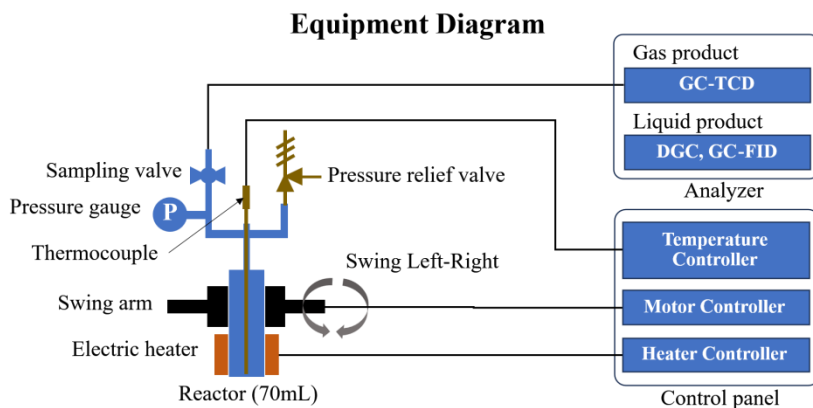


Figure 1 Equipment diagram of oscillatory mixing reactor

Table 1 Reaction conditions under different hydrogen-supply modes

H ₂ Supply Mode	UCO (g)	Catalyst (g)	Temperature (°C)	Holding time (h)	Initial H ₂ pressure (MPa)	H ₂ input/mol UCO	FA added (g)
Catalyst (C)	6.0	0.6	320/350	1	0.0	None	0
C+H ₂	6.0	0.6	320/350	1	0.9	3 mol H ₂	0
C+FA	6.0	0.6	320/350	1	0.0	None	2.2
C+H ₂ +FA	6.0	0.6	320/350	1	0.9	3 mol H ₂	1.1

The amount of gas produced was estimated using an overall mass-balance approach. The reactor and its contents were weighed before and after reaction, and the gas mass was calculated from the difference after considering the recovered liquid and solid fractions. Therefore, the reported gas yield should be interpreted as a mass-balance-based estimate rather than a direct gas-collection measurement. This value was used as a comparative indicator of gas formation among the different hydrogen-supply modes.

Catalytic performance was evaluated from recovered liquid yield, boiling-range distribution, hydrocarbon carbon-number distribution, and gas composition. SimDist classified the liquid products into naphtha (IBP–200°C), kerosene (200–250°C), diesel (250–370°C), and residue (>370°C), while GC-FID and GC-TCD were used for carbon-number distribution and gas-phase composition, respectively. CO and CO₂ were used only as supporting pathway indicators because FA decomposition can also generate these gases.

Results and Discussion

Liquid Yield and Temperature Effect

The effect of reaction temperature was first evaluated by comparing the liquid products obtained at 320°C and 350°C under the four hydrogen-supply modes (

Table 2) Overall, increasing the reaction temperature from 320°C to 350°C improved the extent of liquid-phase upgrading, particularly in terms of distillable product formation and residue suppression. In the C mode, the recovered product yield increased from 38.78% to 53.32%. Similar improvements were observed in the C+H₂ and C+FA modes as display in

Table 2, Although the C+H₂+FA mode showed a slightly lower gravimetric product yield at 350°C than at 320°C, the residue was almost completely suppressed, decreasing from 0.52 g to 0.04 g.

Table 2 Gravimetric recovered liquid yield and fraction weights under different modes

Liquid	H ₂ Supply Mode							
	Catalyst (C)		C+H ₂		C+FA		C+H ₂ +FA	
	320°C	350°C	320°C	350°C	320°C	350°C	320°C	350°C
UCO (g)	6.02	6.08	6.02	6.02	6.02	6.02	6.00	6.09
Product (g)	2.33	3.24	2.87	3.31	2.58	3.21	3.22	3.09
Naphtha (g)	0.54	0.99	0.86	1.33	0.91	1.52	1.40	1.78
Kerosene (g)	0.32	0.51	0.50	0.61	0.56	0.64	0.65	0.61
Diesel (g)	1.47	1.75	1.51	1.38	1.10	1.05	1.16	0.70
Product yield (%)	38.78%	53.32%	47.60%	55.07%	42.78%	53.37%	53.67%	50.68%
Residue (g)	1.16	0.90	1.20	0.58	0.53	0.29	0.52	0.04
Total yield (%)	57.97%	68.09%	67.61%	64.78%	51.66%	58.14%	62.33%	51.40%

The SimDist results in **Table 3** further support the stronger upgrading effect at 350°C. For all reaction modes, the distillable product fraction increased when the temperature was raised from 320°C to 350°C. The product yield calculated from the SimDist boiling-range distribution increased from 66.90% to 78.30% in the C mode, and also the same trend in other modes. Especially in C+H₂+FA mode, increased from 86.10% to 98.60%.

At the same time, the residue fraction decreased markedly at 350°C, suggesting enhanced conversion of heavy oxygenated or partially converted intermediates. Previous studies have shown that increasing temperature promotes further conversion of triglyceride-derived and oxygenated species and, under more severe conditions, secondary cracking toward lighter hydrocarbons [1, 2]. Accordingly, the lower residue accompanied by increased naphtha-range products observed at 350°C suggests that the higher temperature promoted not only deeper conversion but also secondary product lightening.

Liquid Yield and Product Distribution

Based on the gravimetric results in **Table 3** increasing the reaction temperature from 320°C to 350°C generally improved the liquid product yield in the C, C+H₂, and C+FA

modes. This suggests that the higher temperature promoted the conversion of UCO-derived heavy intermediates into liquid-phase products. However, the C+H₂+FA mode did not follow this trend, showing a slightly lower liquid yield at 350°C than at 320°C. This result suggests that the combined C+H₂+FA condition may have increased the reaction severity beyond liquid-product stabilization. In the closed reactor, FA-derived gas formation and the resulting pressure build-up may have further promoted conversion of liquid intermediates into lighter volatile or gaseous products.

At 350°C, the C, C+H₂, and C+FA modes produced comparable liquid product yields of 53.32%, 55.07%, and 53.37%, respectively. Therefore, hydrogen supply did not strongly increase total liquid production under the present conditions. Instead, the main difference among the modes was observed in the distribution of liquid fractions. The C mode retained the largest diesel-range product mass, whereas C+H₂ and C+FA shifted part of the liquid toward lighter fractions. The C+H₂+FA mode showed the strongest naphtha formation and the lowest diesel-range product mass, indicating a more severe redistribution of the liquid product.

Table 3 SimDist-derived boiling-range distribution of liquid products under different H₂-supply modes

Liquid	H ₂ Supply Mode							
	Catalyst (C)		C+H ₂		C+FA		C+H ₂ +FA	
	320°C	350°C	320°C	350°C	320°C	350°C	320°C	350°C
Naphtha	15.40	23.80	21.20	34.10	29.30	43.50	37.50	56.80
Kerosene	9.30	12.20	12.20	15.60	18.00	18.40	17.50	19.40
Diesel	42.20	42.30	37.00	35.30	35.50	29.90	31.10	22.40
Residue	33.10	21.70	29.60	15.00	17.20	8.20	13.90	1.40
Product yield	66.90	78.30	70.40	85.00	82.80	91.80	86.10	98.60

Boiling-range Shift, Residue Reduction

SimDist analysis further clarifies how temperature and hydrogen-supply mode affected the boiling-range distribution of the liquid products. Compared with 320°C, operation at 350°C consistently increased the distillable fraction below 370°C and reduced the residue fraction in all reaction modes. This indicates that the higher temperature promoted the conversion of heavy oxygenated or partially converted compounds into lower-boiling liquid fractions. The effect was most pronounced in the C+H₂+FA mode, where the residue fraction decreased from 13.9% at 320°C to only 1.4% at 350°C.

At 350°C, the C mode retained the highest diesel-range fraction but also showed the largest residue fraction, indicating partial upgrading with limited heavy-fraction conversion. H₂ addition reduced the residue fraction and increased the distillable product fraction, but did not improve diesel-range preservation. FA-containing modes produced a stronger shift toward lower-boiling products. In particular, the C+H₂+FA mode gave the highest distillable fraction of 98.6% and showed the strongest increase in naphtha-range products. This strong light-fraction formation may be partly associated with the higher effective severity created by FA decomposition. In a closed reactor, the formation of H₂, CO₂, and CO can increase the internal pressure and alter the vapor–liquid–solid reaction environment, thereby promoting further conversion of heavy intermediates toward lower-boiling products.

Overall, the SimDist results reveal a clear trade-off between residue suppression and diesel-range preservation. Higher temperature and

FA-assisted operation enhanced heavy-fraction conversion, but this improvement was accompanied by product lightening. Therefore, the key optimization target should not be maximum conversion alone, but controlled redistribution toward the most valuable product window.

Carbon-number Distribution

GC-FID analysis was used to evaluate whether the liquid products retained the carbon-number range expected from UCO-derived fatty acids. The original UCO feed was dominated by C₁₈ and C₁₆ fatty-acid species, mainly oleic acid (C18:1), palmitic acid (C16:0), linoleic acid (C18:2), and stearic acid (C18:0). Therefore, if deoxygenation proceeded mainly through HDO, DCO₂, or DCO with limited secondary cracking, the hydrocarbon products would be expected to remain largely in the C₁₅–C₁₈ range.

However, **Figure 2** shows that the liquid products were distributed over a lighter carbon-number region. At 350°C, the C mode produced hydrocarbons mainly in the C₆–C₁₆ range, while the C+H₂, C+FA, and C+H₂+FA modes showed stronger contributions of lighter hydrocarbons. This indicates that oxygen removal was accompanied by carbon-chain cleavage, especially under H₂- and FA-assisted conditions.

The 320°C results provide a useful comparison for interpreting this trend. At the lower temperature, the shift toward lighter hydrocarbons were less pronounced, suggesting that secondary cracking was less severe. Therefore, the lighter carbon-number distribution observed at 350°C was not only a

result of hydrogen-source selection, but also reflected the higher reaction severity caused by temperature.

Overall, the GC-FID results support the SimDist interpretation that the reaction did not simply preserve C_{16}/C_{18} -derived hydrocarbons in the diesel-relevant C_{15} – C_{18} range, but shifted toward lighter hydrocarbons, especially under FA-assisted operation. Therefore, the substantial formation of hydrocarbons below C_{15} observed in this study cannot be explained by deoxygenation alone and indicates additional C–C bond cleavage or secondary cracking. Similar formation of lighter hydrocarbons at increased reaction severity has been reported for Ni-based deoxygenation systems [1, 12].

Product-window Shift, Diesel Retention

From a product-window perspective (**Figure 3**), the temperature comparison shows a clear trade-off between stronger upgrading and diesel-range preservation. At 320°C, the diesel-range fraction was generally better retained, whereas increasing the temperature to 350°C promoted a stronger shift toward lighter fractions. This indicates that higher reaction severity improved heavy-fraction conversion but reduced the ability to preserve the diesel product window.

At 350°C, the diesel-range fraction decreased progressively from 42.3% in the C mode to 35.3% in C+H₂ mode, 29.9% in C+FA mode, and 22.4% in C+H₂+FA mode. In the same sequence, the naphtha-range fraction

increased from 23.8% to 56.8%. This trend shows that H₂ and FA did not enhance diesel-range preservation under the present conditions. Instead, they redirected the product slate toward lighter hydrocarbon fractions. For the C+FA and C+H₂+FA modes, this product-window shift may not be caused by hydrogen-donor chemistry alone. FA decomposition also generated gaseous products, which increased the internal pressure under the closed batch condition. This pressure build-up may have intensified the reaction environment and contributed to secondary cracking or redistribution toward naphtha-range products.

The moderate increase in kerosene-range products also suggests some movement toward middle-distillate formation. However, the dominant redistribution was toward the naphtha range rather than selective kerosene formation. Therefore, the main limitation of the current operating window was not insufficient conversion of heavy material, but excessive light-product formation and insufficient diesel retention.

Overall, the results indicate that future optimization should focus on moderating reaction severity rather than simply increasing conversion. For diesel-oriented production, lower temperature or reduced donor severity may be beneficial. However, if the target is broadened to include kerosene- and naphtha-range renewable products, the lighter fractions may also be considered as part of the overall product value.

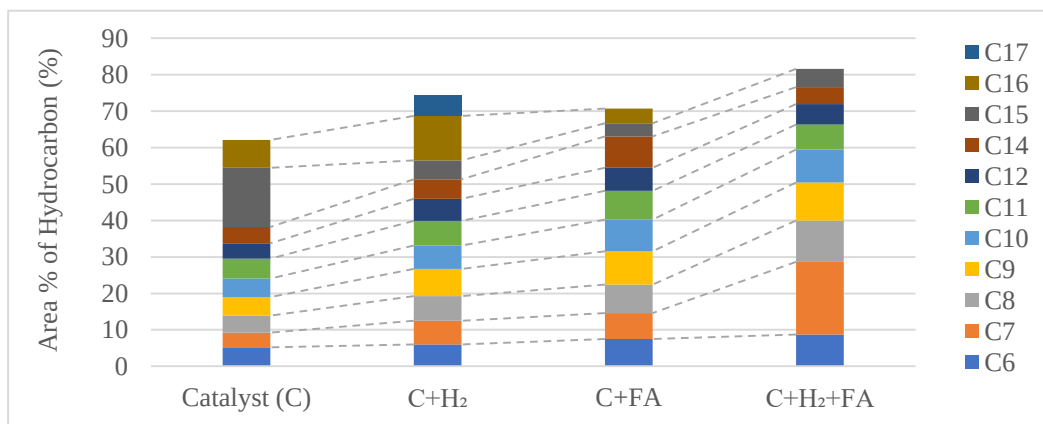


Figure 2 GC-FID-derived hydrocarbon distribution of liquid products at 350°C under different modes

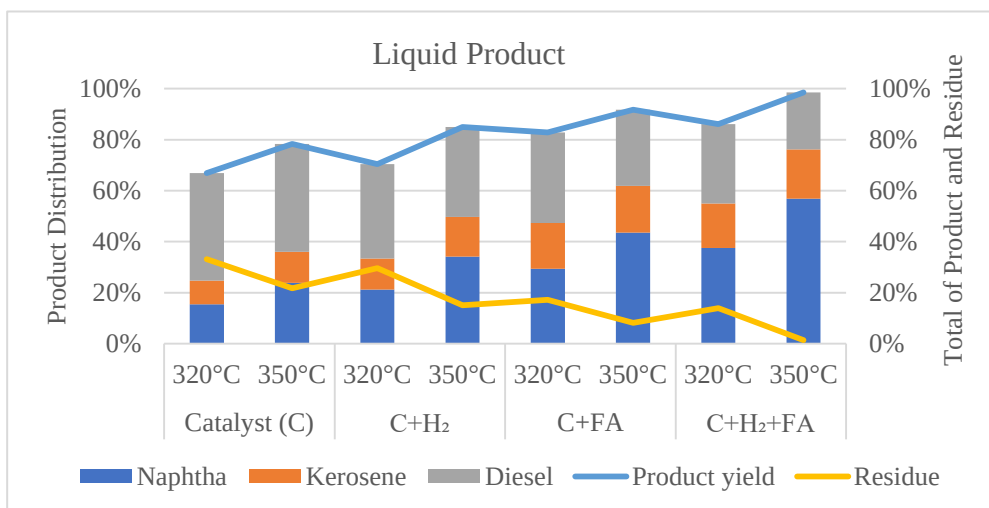


Figure 3 Hydrocarbon distribution of liquid products under different H₂-supply modes
Note: The product name refers from the range of boiling point

Gas-phase and Pathway Interpretation

Gas-phase analysis (**Figure 4**) provides additional evidence for interpreting the liquid-product trends discussed above. Compared with 320°C, the 350°C condition generally produced stronger CO and CO₂ formation, indicating that the higher temperature intensified oxygen-removal and gas-forming reactions.

At 350°C, the C mode produced CO-rich gas even without external H₂ or formic acid. This result suggests that the multifunctional catalyst itself promoted CO-forming deoxygenation pathways, particularly decarbonylation. The low CO₂/CO ratio in this mode further indicates that DCO was more dominant than CO₂-forming decarboxylation under catalyst-only operation.

The occurrence of CO-rich gas under H₂-free conditions is consistent with previous studies showing that Ni/MgO–Al₂O₃-type catalysts can promote non-hydrogenative deoxygenation of fatty acids through DCO/DCO₂ pathways [9, 10]. In the present catalyst, the predominance of CO over CO₂ suggests that the reaction network was more strongly biased toward CO-forming pathways under the C mode condition.

When H₂ was introduced in the C+H₂ mode, CO formation was not fully suppressed. This indicates that the available H₂ under the present condition was insufficient to shift the

reaction network completely toward hydrodeoxygenation. Therefore, DCO remained an important pathway even in the presence of external H₂. This result supports the concept that the present system should be interpreted as controlled low-H₂ deoxygenation rather than HDO-dominant conversion.

For FA-containing modes, both CO and CO₂ increased markedly at 350°C. However, these gases cannot be assigned only to UCO-derived deoxygenation because formic acid can decompose through two competing routes: dehydrogenation to H₂ and CO₂, and dehydration to CO and H₂O. Therefore, CO and CO₂ in the C+FA and C+H₂+FA modes may originate from both UCO conversion and FA decomposition. This makes the CO₂/CO ratio useful as a supporting indicator, but not as a direct quantitative measure of DCO₂/DCO selectivity. In addition to changing the chemical pathway, FA decomposition may also have changed the physical reaction environment. The generation of gaseous products in the closed batch reactor caused pressure build-up, which may have increased the effective reaction severity. This pressure-assisted severity could promote further transformation of heavy oxygenated intermediates and partially converted liquid products, leading to stronger residue suppression but also greater formation of naphtha-range hydrocarbons.

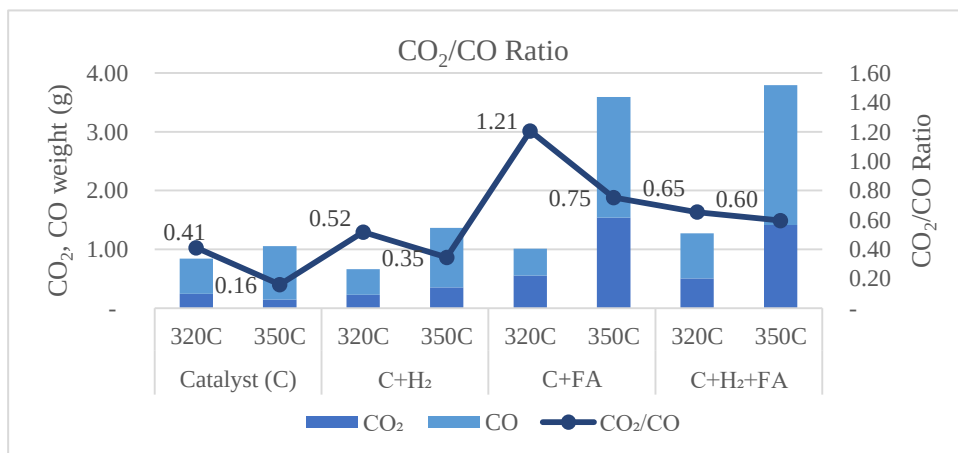


Figure 4 Gas-phase composition determined by GC-TCD, pathway-related indicators.

Note: Total gas yield was estimated separately by overall mass difference

Overall, the gas results are consistent with the liquid-product analysis. The 320°C data represent a lower-severity reference, whereas the 350°C data more clearly show intensified CO_x formation, stronger residue suppression, and greater product lightening. Thus, the gas-phase evidence supports the interpretation that donor-assisted operation promoted deeper conversion not only through chemical donor effects, but also through pressure-related reaction severity and secondary redistribution of the liquid products.

Product-value Implication

In term of product value, it should be interpreted a redistribution of renewable hydrocarbon fractions with different potential downstream applications. Beyond maximizing diesel-range selectivity, the liquid product should be evaluated from an overall product-value perspective. UCO-derived liquid hydrocarbons can potentially be fractionated into diesel-range hydrocarbons for renewable diesel, kerosene-range hydrocarbons as SAF-relevant intermediates or blending-oriented fractions, and naphtha-range hydrocarbons as renewable feedstock for petrochemical or circular plastic applications.

This perspective may become increasingly important in the future as biogenic kerosene- and naphtha-range hydrocarbons gain more relevance in low-carbon fuel and circular carbon markets. Aviation fuel development is

moving toward certified low-carbon and biogenic components under frameworks such as ICAO/CORSIA, while the petrochemical sector is also seeking renewable and circular carbon feedstocks for plastics and chemical production. If properly separated, upgraded, and certified, these fractions may become value-added renewable product streams.

Thus, future optimization should not focus only on maximizing diesel yield, but should also consider product-window allocation. Depending on market demand and downstream upgrading options, the optimal operating condition may be the one that provides the highest overall value from a controlled balance of renewable diesel, SAF-relevant kerosene, and renewable naphtha, rather than the highest diesel fraction alone.

Conclusions

The multifunctional Ni-MgO-Ce_{0.6}Zr_{0.4}O₂/γ-Al₂O₃ catalyst was applied for UCO deoxygenation under different hydrogen-supply modes at 320°C and 350°C. The comparison between the two temperatures showed that 320°C provided a lower-severity reference, where diesel-range products were generally better preserved, while 350°C promoted stronger liquid-phase upgrading, higher distillable-product formation, and more effective residue suppression. Therefore, the temperature effect revealed a clear trade-off

between diesel-range preservation and heavy-fraction conversion.

At 350°C, H₂- and FA-assisted modes increased the distillable liquid fraction and strongly reduced residue. However, this improvement was accompanied by a shift of the product distribution toward lighter naphtha- and kerosene-range fractions. The diesel-range fraction decreased from the C mode to the C+H₂+FA mode, indicating that the current donor-assisted condition increased reaction severity but did not preserve the diesel product window. GC-FID carbon-number distribution further confirmed that the products were not simply retained in the C₁₅–C₁₈ diesel-relevant range, but were shifted toward lighter hydrocarbons.

Gas-phase analysis supported the interpretation of CO- and CO₂-forming pathways. The catalyst mode produced CO-rich gas even without external H₂ or FA, suggesting that the catalyst can promote decarbonylation under low-H₂ conditions. Moreover, FA-derived gas formation may have increased the internal reactor pressure, thereby contributing to higher reaction severity, residue suppression, and product lightening. Therefore, gas-phase indicators should be interpreted together with liquid yield, boiling-range distribution, and carbon-number distribution.

Overall, the results show that DCO/DCO₂ can be useful low-H₂ deoxygenation pathways, but only if secondary cracking and excessive light-product formation are controlled. The optimization target should therefore not be limited to maximum conversion or maximum diesel yield alone. Future process development should consider product-window allocation and overall product value, including renewable diesel-range hydrocarbons, SAF-relevant kerosene-range fractions, and renewable naphtha for circular petrochemical applications.

Further work should focus on reaction control and analytical validation. Key variables include reaction temperature, residence time, catalyst loading, H₂ pressure, FA dosage, and H₂:FA ratio. Additional GC-MS analysis, oxygenate quantification, and improved gas quantification are required to confirm pathway contribution and product stability. A more selective reduced-H₂ window should balance

residue suppression, diesel retention, and the total value of fractionated renewable products.

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