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Effects of CoMo/ γ -Al₂O₃ Catalysts on Product Hydrocarbon and Phenol Distribution during Hydrodeoxygenation of Oxidized Bio-Oil in a Batch Reactor

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Abstract: Hydrodeoxygenation is an essential process for producing liquid transportation fuels. In this study, the effects of CoMo/ γ -Al₂O₃ catalysts form and loading ratio on the hydrodeoxygenation upgrading of bio-oil were investigated in a batch reactor. Raw bio-oil was first oxidized with hydrogen peroxides and oxone to obtain the oxidized bio-oil with reduced levels of aldehydes and ketones, increasing the organic liquid yield during hydrodeoxygenation by suppressing the coke formation. CoMo/ γ -Al₂O₃ was selected as the catalyst because of its low cost and commercial availability. The effect of the reduction and sulfidation of CoMo/ γ -Al₂O₃ catalyst on the hydrodeoxygenation of the oxidized bio-oil was compared. The effect of the catalyst loading ratio on bio-oil hydrodeoxygenation using sulfided CoMo/ γ -Al₂O₃ catalysts was also investigated. The research results showed that the sulfided CoMo/ γ -Al₂O₃ catalyst facilitated the formation of hydrocarbons, while the reduced CoMo/ γ -Al₂O₃ catalyst produced more phenols in the organic liquids. Moreover, a high sulfided catalyst loading ratio promoted the formation of hydrocarbons.

Keywords: oxidized bio-oils; hydrodeoxygenation; phenols; hydrocarbons; CoMo/ γ -Al₂O₃

1. Introduction

In the past decades, rapid industrialization and population growth have caused severe environmental issues such as global warming, clean water crisis, and resource depletion [1–8]. To achieve the goal of carbon neutrality, the development of bio-based materials and bioenergy as an alternative to fossil-based materials and energies has been attracting researchers' interest [9–15]. Due to its carbon value, abundance, and renewability, lignocellulosic biomass is a potential resource for biofuel and biochemical production via thermochemical conversion technologies such as high-pressure liquefaction and atmospheric slow/fast pyrolysis, as well as further hydroprocessing [16,17].

Bio-oil produced via the thermal decomposition of biomass in the absence of air is a renewable liquid fuel with the higher heating value (HHV) of 17–18 MJ/kg [18,19]. However, the presence of water and diverse oxygen-containing chemical compounds make bio-oil be viscous and acidic, and reduce its HHV and thermal stability [20–24]. Therefore, the upgrading of bio-oil to reduce its water, ketone, and acid compound contents and increase its HHV and stability is crucial in order to improve its applicability as a

transportation fuel. The reactive components (ketones, aldehydes, sugars, etc.) cause polymerization and aggregation reactions during bio-oil production and in following refinery processes, which lead to the coking issue and greatly decrease the workability and service life of reactors [25–27]. Therefore, the pretreatment of raw bio-oil to remove its ketone and aldehyde content before upgrading is essential.

Recently, oxidation with hydrogen peroxide and oxone has been recognized as a simple and effective method for raw bio-oil pretreatment because it can be conducted at low temperatures (<100 °C) and ambient pressure. During hydrogen peroxide/oxone oxidation, the carbonyl compounds (aldehydes and ketones) and a portion of the alcohols in raw bio-oil can be oxidized to acids, producing oxidized bio-oil with good workability for following upgrading process [28]. With the addition of butyric anhydride in the hydrogen peroxide/oxone oxidation process, water in the raw bio-oil can be converted to butanoic acid methyl esters, which can be directly converted to hydrocarbon fuels during the following upgrading process without water removal [29].

Many conversion methods have been applied to upgrade bio-oils to high-quality fuels, including catalytic hydroprocessing [30,31], catalytic reforming [32], catalytic pyrolysis [33], esterification [34], and supercritical treatment [35,36]. Catalytic hydrodeoxygenation has been the most widely employed method, using a variety of heterogeneous catalysts in the presence of pressurized hydrogen [37].

CoMo/ γ -Al₂O₃- and NiMo/ γ -Al₂O₃-based catalysts have been widely used for bio-oil hydrodeoxygenation because of their cost-effectiveness and commercial availability. Parapati [29] found that the sulfided CoMo/ γ -Al₂O₃ catalyst provided a yield of hydrocarbons that was 10 times higher than that of the reduced CoMo/ γ -Al₂O₃ catalyst. Sulfided CoMo/ γ -Al₂O₃ and NiMo/ γ -Al₂O₃ catalysts can improve the reactivity of methyl heptanoate and guaiacol with the formation of methanethiol but decrease that of phenol. Moreover, the presence of sulfur compounds in the gas phase during hydrodeoxygenation can reduce the hydrogenation activity of the sulfided catalyst, and thereby increase the selectivity towards C₇/C₆ hydrocarbon [38]. In addition to the pretreatment of the catalyst, the selectivity of product is also affected by the reaction conditions. For instance, in the hydrotreating of methyl esters with NiMo/ γ -Al₂O₃ catalyst, severe reaction conditions mainly yielded kerosene, while mild conditions produced a more renewable diesel fraction [39].

In our previous study, Ni-based catalysts were applied for the hydrodeoxygenation of oxidized bio-oil to produce pure hydrocarbon in a two-stage batch process. The products were a mixture of gasoline, diesel, and jet fuel [18,19]. It was also found that the oxidized bio-oil increased the yield of hydrocarbons and reduced the coking amounts. In addition, the hydrodeoxygenation of the pretreated bio-oils was evaluated using sulfided CoMo/ γ -Al₂O₃ catalyst through a fixed-bed continuous process. Both oxidation and hydrodeoxygenation were found to decrease the coke formation and increase the working life of catalysts for bio-oil upgrading. However, although the previous study used a fixed catalyst loading for bio-oil upgrading to hydrocarbons, the effect of catalyst form and loading ratio on the product distribution and hydrocarbon selectivity is still unclear.

In this research, the research routes are described in Scheme 1. Firstly, we compared the form of catalyst (i.e., sulfidation and reduction) on the distribution of hydrocarbons and phenol in the organic liquids of the bio-oil upgrading products. Moreover, we investigated the effect of sulfided CoMo/ γ -Al₂O₃ catalyst loading ratio on the types and concentrations of chemicals in the produced organic products from oxidized bio-oil hydrodeoxygenation. This study provides useful information for bio-oil upgrading through oxidation and then CoMo/ γ -Al₂O₃ hydrodeoxygenation, which can be used for bio-oil storage and transportation, as well as refinery design.

Scheme 1. Raw bio-oil was oxidized and then subjected to hydrodeoxygenation.

2. Materials and Methods

2.1. Materials

CoMo/ γ -Al₂O₃ catalyst was purchased from Alfa Aesar (U.S.). Hydrogen (H₂), helium (He), and 5% H₂/Ar gases were supplied by NexAir (U.S.). Carbon disulfide (CS₂, Certified ACS Reagent Grade $\geq 99.9\%$), cyclohexane (Certified ACS Reagent Grade $\geq 99.0\%$), hydrogen peroxide (30 wt% solution in water, Certified ACS 30.0 to 32.0%), isopropanol (99.9%, HPLC Grade), dichloromethane (Stabilized/Certified ACS), and oxone were purchased from Fisher Scientific. All chemicals were used without further purification.

2.2. Bio-Oil Production and Oxidation

Loblolly pine (*Pinus taeda*) was ground and sieved to a particle size range of 0.5–4 mm and then oven-dried to a moisture content below 5 vol.%. Raw bio-oil was produced at 450 °C in a 7 kg/h auger-fed pyrolysis reactor under a nitrogen atmosphere. To obtain raw bio-oil [40], the bio-oil aqueous fraction vapors were condensed in four condensers. The condenser temperature was maintained below the water vaporization temperature. All bio-oil oxidation treatments were performed in a stainless-steel 1.8 L Parr batch autoclave reactor, equipped with an overhead magnetic stirrer. Oxidized bio-oil was produced by treating raw bio-oil with 10 wt% hydrogen peroxide and 5 wt% oxone for 90 min in a stirred Parr batch reactor at ambient temperature and pressure [18,19].

2.3. CoMo/ γ -Al₂O₃ Catalyst Reduction and Sulfidation

The reduction of CoMo/ γ -Al₂O₃ catalyst was conducted in a fixed-bed continuous reactor using 5% H₂/Ar for 4 h at 500 °C at a flow rate of 100 mL/min. Meanwhile, the CoMo/ γ -Al₂O₃ catalysts were sulfided in a fixed-bed continuous reactor using 2 vol.% CS₂ in cyclohexane as a sulfiding agent. The sulfidation process was performed for 4 h at 350–375 °C under 750 psig H₂ pressure. The sulfiding agent was passed through the catalyst bed at a liquid hour space volume of 1 h^{−1} while the H₂ flow rate was maintained at a gas hour space velocity of 2 h^{−1}. After 4 h of reaction, the catalyst bed was swept with He for 3–4 h to remove any residual sulfiding agent [41].

2.4. Hydrodeoxygenation of Oxidized Bio-Oil

Hydrodeoxygenation of oxidized bio-oil was performed in the batch reactor using reduced and sulfided CoMo/ γ -Al₂O₃ catalysts, respectively. All hydrodeoxygenation reactions were performed in the presence of catalysts for 3 h at a temperature of 400 °C and an initial hydrogen pressure of 1000 psig. Products collected from the batch reactor were separated by centrifugation at 4000 rpm for 1 h. The top phase (i.e., organic liquids) was collected for yield calculation and further analysis.

2.5. Characterization

2.5.1. Physical Properties

The properties of raw bio-oil, oxidized bio-oil, and organic liquids were characterized for water content, HHV, acid value, and elemental analysis. Water content was determined by the Karl Fisher titration method using a Cole-Parmer Model C-25800-10 titration apparatus (Thermo Fisher Scientific Inc., Waltham, MA, USA). HHV was determined by a

Parr 6200 oxygen bomb calorimeter (Parr Instrument Co., Moline, IL, USA) according to the ASTM D240 method. Acid value was obtained according to the ASTM D664 method. Carbon, hydrogen, nitrogen, and oxygen (by subtraction) contents were measured by a CE-440 Elemental Analyzer (Exeter Analytical, North Chelmsford, MA, USA) with acetanilide as the standard. Therefore, the mass balance of C, H, O, and N elements were not calculated separately (C = 71.09%, H = 6.71%, N = 10.36%, and H = 11.84%) [18,19,42,43]. For all of the above analysis, the ASTM standard methods were applied and the analytical results are presented using one-time analytical data, and the reliability of the analytical results has been confirmed in many published research results [18,19,42,43]. For S element, it is possible that there was some S leaching in the liquid products; previous research has confirmed the presence of 0.00028–0.0059% in the organic liquid product of the fixed continuous reaction [41].

2.5.2. Gas Chromatography-Mass Spectrometry

The volatile and semi-volatile components of raw and oxidized bio-oil samples, as well as organic liquids, were analyzed by a Hewlett Packard 5971 series gas chromatograph-mass spectrometer (GC/MS). The injector temperature was 270 °C. A 30 m × 0.32 mm internal diameter × 0.25 µm film thickness silica capillary column, coated with 5% phenyl-methylpolysiloxane, was used at an initial temperature of 40 °C for 4 min followed by heating at 5 °C/min to a final temperature of 280 °C for 15 min. The mass spectrometer employed a 70 eV electron impact ionization mode, a source-detector temperature of 250 °C, and an interface temperature of 270 °C. About 0.2 g of the raw bio-oil and oxidized bio-oil was dissolved in 10 mL methanol while about 0.2 g of organic liquid product was dissolved in 10 mL dichloromethane, respectively [43,44].

2.5.3. Gas Chromatography

Exit gases were collected into a 1 L Tedlar bag and analyzed using a gas chromatograph (SRI 8610C) equipped with thermal conductivity (TCD) and flame ionization (FID) detectors. A ShinCarbon ST 100/120 (2 m × 1 mm ID × 1/16 inch OD silico) packed column and a MXT-1 (60 m × 0.53 mm ID × 5.00 µm) capillary column were employed for the separation of inorganic gases and light hydrocarbons [19].

3. Results and Discussion

3.1. Physical Properties of Raw Bio-Oil, Oxidized Bio-Oil, and Organic Liquids

Raw bio-oil contains many oxygen-containing compounds, such as aldehydes and ketones. The direct hydrodeoxygenation of raw bio-oil at 400 °C cannot produce organic liquids, but forms coke due to the polymerization of these oxygen-containing compounds. In the current research, organic liquids were all produced from the hydrodeoxygenation of oxidized bio-oil. Table 1 compares the physical properties of raw bio-oil, oxidized bio-oil, and organic liquids. In comparison with both raw (28.4 vol.%) and oxidized bio-oils (30.9 vol.%), organic liquids had a much lower water content (0.53–5.06 vol.%). In addition, organic liquids exhibited a much higher number of HHV (33–45 MJ/kg) than those of raw bio-oil (14.75 MJ/kg) and oxidized bio-oils (misfire due to high water content).

Organic liquids also had the lowest acid value of less than 6 mg KOH/g compared to raw bio-oil (95.2 KOH/g) and oxidized bio-oil (179.5 mg KOH/g). The high acid value for raw bio-oil was due to its initial high carboxylic acid content, which increased during the peroxide/oxone oxidation process [28,29]. The low acid values of all obtained organic liquids indicated the high efficiency of both the reduced and sulfided CoMo/ γ -Al₂O₃ catalysts for the hydrodeoxygenation of oxidized bio-oil [29].

Table 1. Physical properties of raw bio-oil, oxidized bio-oil, and organic liquids.

Properties	Raw Bio-Oil	Oxidized Bio-Oil	Organic Liquids				
	/	/	^a RC-10	^b SC-5	^b SC-8	^b SC-10	^b SC-15
HHV, MJ/kg	14.75	Misfire	40	33.83	37.27	43.31	44.65
Total acid number, mg KOH/g	95.2	179.5	0.55	5.54	3.25	0.55	0.55
Water content, vol. %	28.4	30.9	5.06	2.62	2.71	1.64	0.53
Oil phase weight, g	/	/	18.2	17.65	15.3	14.25	13.1
Water phase weight, g	/	/	50.5	53.35	50.6	40.45	56.1
Yield, wt %	/	/	20	19	17	16	14
Carbon, wt %	43.6	31.8	80.81	85.38	83.14	85.29	87.25
Hydrogen, wt %	7.8	7.8	10.27	11.08	11.18	11.75	12.35
Nitrogen, wt %	0.20	0.02	1.06	0.13	0.16	0.85	0.12
Oxygen, wt %	48.4	60.64	7.85	3.41	5.52	2.10	0.28

Note: ^a RC-10 means organic liquids produced from oxidized bio-oil upgrading with 10 wt% reduced CoMo/ γ -Al₂O₃ as the catalyst;

^b SC-X means organic liquids produced from oxidized bio-oil upgrading with sulfided CoMo/ γ -Al₂O₃ as the catalyst; X represents the catalyst loading ratio (wt%).

The elemental analysis results in Table 1 indicate that the organic liquid exhibited significantly higher carbon content (>80 wt%) compared to the 43.6 and 31.8 wt% for raw bio-oil and oxidized bio-oil, respectively. Moreover, the oxygen contents of organic liquids ranged from 0.28 wt% to 7.85 wt% depending on the catalyst used, which are much lower than those of raw bio-oil (48.4 wt%) and oxidized bio-oil (60.64 wt%). The high carbon content and low oxygen content of organic liquids were responsible for their HHV. The improved basic physical properties of the organic liquids indicated that hydrodeoxygenation occurred, and the effects were comparable to the reported results [28].

Although reduced and sulfided CoMo/ γ -Al₂O₃ catalysts worked well for the hydrodeoxygenation of oxidized bio-oil, the sulfided catalysts had higher efficiency than the reduced catalyst, which was consistent with other reported work [29,41]. Specifically, for the sulfided catalyst, the HHV of the resulting organic liquids was between 33 and 45 MJ/kg, and the HHV increased with the increase in the catalysts' loading ratio. The acid value of the organic liquids decreased from 5.5 to 0.55 mg KOH/g as the sulfided catalyst loading ratio increased from 5 to 15 wt%. The water and oxygen contents of the resulting organic liquids were in the range of 0.53–2.71 vol.% and 0.28–5.52 wt%, respectively, and exhibited a decreasing trend with the increase in the loading ratio of sulfided CoMo/ γ -Al₂O₃ catalysts. The yield of organic liquid also decreased in response to the increase in the catalyst. Overall, the increase in sulfided CoMo/ γ -Al₂O₃ catalyst loading ratio improved the properties of the obtained organic liquids. Moreover, in comparison with the reduced CoMo/ γ -Al₂O₃ catalysts, organic liquids obtained from sulfided CoMo/ γ -Al₂O₃ catalysts hydrodeoxygenation showed better properties in terms of HHV, water content, carbon content, and oxygen content. It could be included that the efficiency of hydrodeoxygenation depended on the form of the CoMo/ γ -Al₂O₃ catalyst as well as the catalyst loading ratio. The form of the catalysts, the method of pretreatment of the bio-oil, and the input of hydrogen concentration had a significant influence on the organic liquid products' distribution, which have also been verified in previous research results [18,42].

3.2. GC/MS Analysis of Raw Bio-Oil, Oxidized Bio-Oil, and Organic Liquids

To further investigate the composition of organic phases in raw bio-oil and oxidized bio-oils, as well as organic liquids produced from hydrodeoxygenation of oxidized bio-oil, GC/MS analysis was conducted and the results are exhibited in Table 2 and Figure 1. The main components of raw bio-oil were phenols, acid, aldehydes, ketone, and other oxygenates (Table 2). After oxidation, the aldehydes and ketone in raw bio-oil, known to catalyze polymerization and aggregation reactions [41–43], were largely reduced in the oxidized bio-oil. Specifically, the contents of aldehyde and ketone were reduced from 5% and 9% to 3% and 0%, respectively.

Table 2. GC/MS analysis of raw bio-oil, oxidized bio-oil, and organic liquids (%).

Types	Raw Bio-Oil	Oxidized Bio-Oil	^a RC-10 (Organic Liquid)	^b SC-5 (Organic Liquid)	^b SC-8 (Organic Liquid)	^b SC-10 (Organic Liquid)	^b SC-15 (Organic Liquid)
Alkane	/	/	25	37	37	40	58
Benzene	/	/	9	18	8	31	27
Naphthalene	/	/	10	4	1	21	11
Phenol	26	40	49	33	34	8	/
Alcohol	1	6	7	1	9	/	/
Acid	27	26	/	/	/	/	/
Ketone	9	/	/	/	/	/	/
Furfural	1	4	/	/	/	/	/
Aldehyde	5	3	/	/	/	/	/
Other	31	21	/	7	10	/	3

Note: ^a RC-10 means organic liquids produced from oxidized bio-oil upgrading with 10 wt% reduced CoMo/ γ -Al₂O₃ as the catalyst;

^b SC-X means organic liquids produced from oxidized bio-oil upgrading with sulfided CoMo/ γ -Al₂O₃ as the catalyst; X represents the catalyst loading ratio (wt%).

Figure 1. GC/MS analysis of raw bio-oil, oxidized bio-oil, and organic liquids (RC-10 and SC-X) obtained from the hydrodeoxygenation of oxidized oil using different catalysts. Note: ^a RC-10 means organic liquids produced from oxidized bio-oil upgrading with 10 wt% reduced CoMo/ γ -Al₂O₃ as the catalyst; ^b SC-X means organic liquids produced from oxidized bio-oil upgrading with sulfided CoMo/ γ -Al₂O₃ as the catalyst; X represents the catalyst loading ratio (wt%).

The chemical types were almost the same for all of the organic liquids using both reduced and sulfided catalysts, regardless of the catalyst loading ratio. However, the relative concentrations for each chemical component were significantly different. Organic liquids produced using sulfided CoMo/ γ -Al₂O₃ contained 37–58%, 18–31%, 4–21%, 0–33%, and 1–9% of alkanes, benzene, naphthalene, phenol, and alcohol, respectively. And the organic liquids produced using reduced CoMo/ γ -Al₂O₃ contained 25%, 9%, 10%, 49%, and 7% of alkanes, benzene, naphthalene, phenol, and alcohol, respectively. Sulfided catalysts were beneficial for alkane and benzene production, while the reduced catalyst favored phenol production. This indicated that the sulfided CoMo/ γ -Al₂O₃ had a higher hydrodeoxygenation efficiency than the reduced CoMo/ γ -Al₂O₃. Sulfided catalysts resulted in more alkanes and benzene but less phenol, indicating that more phenols were converted to hydrocarbons. Especially when the loading ratio of sulfided catalyst to oxidized bio-oil was more than 10 wt%, the chemical types and amounts were different in terms of phenol, converting all the phenols to hydrocarbons.

The conversion of the oxidized bio-oil to hydrocarbons or phenol depended on many factors. Although the techno-economic aspect of this research was not considered, there was some information reported for reference. For example, there are four major cost considerations in bio-oil hydrodeoxygenation, including raw bio-oil cost, capital cost, hydrogen cost, and relative product value [45]. Furthermore, the National Renewable Energy Laboratory (NREL) reported that the cost of hydrodeoxygenation technology using a hydrogen purchase scenario was lower than the cost of using on-site hydrogen production due to the difference in capital costs of a hydrogen reforming plant [46]. In addition, the Pacific Northwest National Laboratory (PNNL) observed that the hybrid method of fast pyrolysis, hydrotreating, and hydrocracking to produce diesel and gasoline could be financially attractive if the pyrolysis plant was located within an existing refinery in order to reduce the capital costs of the hydrotreating unit and the steam reforming unit [47].

3.3. GC Analysis of the Exit Gas Component

Table 3 gives the GC analysis of the exit gas compositions from the hydrodeoxygenation of oxidized bio-oil with the reduced and sulfided CoMo/ γ -Al₂O₃ catalysts. All exit gas samples were mainly comprised of variable concentrations of H₂, CH₄, CO, CO₂, and C₂H₆. Catalytic hydrodeoxygenation of oxidized bio-oil in the presence of pressurized H₂ was expected to convert oxygenates to organic liquid products and gaseous hydrocarbons (CH₄, C₂H₆, etc.) as well as carbon oxides (CO, CO₂) by decarbonylation/decarboxylation reactions [19,28]. The high consumption of H₂, ranging from 41 to 47%, and the production of 1–3% CH₄, ~1% CO, 7–11% CO₂, and ~2% C₂H₆ during the deoxygenation step, supported the occurrence of the hydrodeoxygenation process, which was also demonstrated in previous research [19].

Table 3. Hydrodeoxygenation reaction exit gas components analysis by GC.

Catalysts	^a RC-10	^b SC-5	^b SC-8	^b SC-10	^b SC-15
H ₂ /%	52.84	57.09	58.28	53.82	58.06
CH ₄ /%	1.57	1.99	1.13	2.1	2.82
CO/%	1.00	0.71	0.59	0.52	0.65
CO ₂ /%	10.48	8.65	7.16	7.72	8.33
C ₂ H ₆ /%	0.04	0.01	0.03	2.17	2.53

Note: ^a RC-10 means organic liquids produced from oxidized bio-oil upgrading with 10 wt% reduced CoMo/ γ -Al₂O₃ as the catalyst; ^b SC-X means organic liquids produced from oxidized bio-oil upgrading with sulfided CoMo/ γ -Al₂O₃ as the catalyst; X represents the catalyst loading ratio (wt%).

4. Conclusions

We studied the influence of reduced and sulfided CoMo/ γ -Al₂O₃ catalysts as well as sulfided CoMo/ γ -Al₂O₃ catalyst-loading ratio on the hydrodeoxygenation of oxidized bio-oil. The results indicated that organic liquids obtained from the oxidized bio-oil hydrodeoxygenation using both reduced and sulfided CoMo/ γ -Al₂O₃ catalysts had similar physical properties in terms of total acid value, water content, oxygen content, and higher heating value. However, the chemical compositions of organic liquids varied with the form of CoMo/ γ -Al₂O₃ catalyst. Organic liquids produced from sulfided CoMo/ γ -Al₂O₃ catalysts contained more hydrocarbons, while organic liquids resulted from the reduced ones had more phenols. Moreover, a higher loading ratio of sulfided CoMo/ γ -Al₂O₃ catalysts to the oxidized bio-oil facilitated the conversion of the phenol to hydrocarbons.

Author Contributions: Y.L. designed the experiments and wrote the manuscript. H.P. wrote the manuscript and analyzed the results. X.Z. (Xuan Zhou) conducted the results analysis. Z.D. conducted the results analysis. G.L. analyzed the experimental data. X.Z. (Xuefeng Zhang) and J.W. edited the manuscript. C.Z. polished and edited the manuscript. All authors have read and agreed to the published version of the manuscript.

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