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Article

# Production of Sustainable Aviation Fuel by Hydrocracking of *n*-Heptadecane Using Pt-Supported Y-Zeolite-Al<sub>2</sub>O<sub>3</sub> Composite Catalysts

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jet fuel fraction. Further, 0.5Pt/Z(110)35A, which has a composition similar to that of 0.5Pt/Y(100)35A except for the type of zeolite, could not give as high yield of jet fuel as 0.5Pt/Y(100)35A because the rapid conversion to lighter fractions than the jet fuel occurred by the slight increase in the reaction temperature even at a lower temperature range.

## 1. INTRODUCTION

Today, there is a need for clean and carbon-neutral gasoline and diesel production technologies. Among them, research studies on the production of transportation fuel, for example, long-chained hydrocarbons of C15–C18 from biomass fat, are actively conducted.<sup>1–4</sup> Synthesis gas made from biomass and waste plastics can also be used to synthesize long-chain hydrocarbons by the Fischer–Tropsch (FT) process, and successive hydrocracking of them can give transportation fuel fractions with high quality.<sup>5</sup> Thus, the hydrotreatment of fat and the combination of biomass gasification and the FT method are thought to be useful for the production of renewable carbon-neutral fuels.

In recent years, many studies have been reported on the production of jet fuel or other fractions by hydrocracking and isomerization reactions using hydrocarbons from *n*-C15 to *n*-C18 as a model of hydrotreated fat or FT wax, <sup>5-24</sup> biodiesel of fatty acid methyl ester and fats, etc.<sup>25-30</sup> because jet fuel is considered to be highly likely to be liquid in the future due to various factors. The hydrocracking catalyst needs to arrange the cracking and isomerization abilities in order to achieve high selectivity for the intermediate fraction. For this reason, the preparation of catalysts which can regulate cracking activity by changing the type, content, and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of a zeolite in the catalyst has been investigated.<sup>5-25</sup> Although *n*-hexadecane

has usually been used so far, a high yield of jet fuel fraction has not been achieved. Further studies of *n*-heptadecane are very few.<sup>16</sup> *n*-Heptadecane has the melting point of 22 °C, freezes in winter, and is difficult to treat compared to *n*-hexadecane.

The purpose of this study is to selectively obtain sustainable aviation fuel (SAF), the intermediate fraction with the highest economic value, through the hydrocracking of *n*-heptadecane (C17) as a model raw liquid from hydrotreatment of a fat or cracking of FT wax. Al<sub>2</sub>O<sub>3</sub> with mesopores as a matrix component, HY-zeolite, and binder (alumina-sol) were kneaded to prepare a HY-zeolite-Al<sub>2</sub>O<sub>3</sub> composite support. It was found for the first time that hydrocracking of *n*-C17 by the 0.5 wt % Pt/50 wt % HY-zeolite (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 100)-50 wt % Al<sub>2</sub>O<sub>3</sub> composite catalyst gave the C8–C15 fraction with a selectivity of 74% and a conversion of 99% at 295 °C and 0.5 MPa.

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## 2. EXPERIMENTAL SECTION

2.1. Preparation of Pt/Zeolite-Al<sub>2</sub>O<sub>3</sub> Catalysts. HYzeolite  $(SiO_2/Al_2O_3 = 100, HSZ-385HUA, Tosoh), HZSM-5$ zeolite (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 110, Tosoh), Al<sub>2</sub>O<sub>3</sub> (270 m<sup>2</sup>/g, Japan Ketjen), and alumina sol (used as an alumina binder, Cataloid AP-1, JGC Catalyst Chemical) were used to prepare composite supports. A composite support included 50 wt % of a zeolite (3.0 g), 35 wt % of a matrix component Al<sub>2</sub>O<sub>3</sub> (2.1 g) and 15 wt % of alumina binder from alumina-sol (1.2640 g, calculated assuming that 71.2 wt % of alumina binder is included in the alumina-sol). The composite support was prepared using the conventional kneading method. The materials were placed in a mortar, and the ion-exchanged water of about 6 g was dripped until it became a clay-like mass, which was pelletized using a pellet molding tool. The pellets obtained were calcined under the following conditions: air atmosphere, heating rate of 2  $^{\circ}C/$ min, temperature of 500 °C, and the holding time of 3 h. The resulting support was ground using a mortar and sieved to particles with size of 600–355 and 355–125  $\mu$ m in a 1:1 ratio. The composite supports were named as Y(100)35A and ZSM(110)35A, where Y and ZSM are the type of zeolite, 100 and 110 are the  $SiO_2/Al_2O_3$  ratio, and 35A is the 35 wt % content of commercial Al<sub>2</sub>O<sub>3</sub>. 0.5 wt % of Pt was added by the conventional impregnation method using hydrogen hexachloroplatinate(IV) hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, Fuji Film Wako Pure Chemical Industry Co., Ltd.). In to a 200 mL beaker was added the support. H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O dissolved in water was added to the beaker at 25 °C. After 24 h, the solvent was evaporated at 100 °C for 5 h. The resulting powder was calcined under the conditions of air atmosphere, heating rate of 2 °C/min, temperature of 500 °C, and holding time of 3 h. The Pt catalyst was named the Pt/composite support.

**2.2.** Characterization of Pt/Zeolite-Al<sub>2</sub>O<sub>3</sub> Catalysts. The prepared catalyst was analyzed by X-ray diffraction (XRD), N<sub>2</sub> adsorption and desorption measurements, temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD), transmission electron microscopy (TEM), and thermogravimetry-differential thermal analysis (TG-DTA) measurements.

For the XRD measurement, an Ultima IV X-ray diffractometer (Rigaku Corporation) was used. An appropriate amount of sample was placed in a dedicated data holder, pressed against a glass plate, flattened, and measured. The diffractometer used a monochromatic Cu Ka line ( $\lambda = 0.15418$ nm) with a Ni filter, and the measurement conditions were as follows: starting angle, 10°; end angle, 70°; sampling width, 0.0200; scan speed, 1.0000; voltage, 40; current, 20; divergence slit, 2/3°; divergence column-limiting slit, 10.00 mm; scattering slit, 2/3°; light-receiving slit, 0.45 mm; and offset angle, 0.0000.

 $N_2$  adsorption/desorption measurements were performed to investigate the surface area, pore size, pore volume, and pore distribution of the prepared catalyst. A BELPREP-vacII (Japan Bell Corporation) was used for pretreatment, and a BELSORPmini (Japan Bell Co., Ltd.) was used for the measurement. Approximately 0.07 g of sample was used for the measurement. The adsorption temperature of  $N_2$  was 77 K, the surface area was determined by the Brunauer–Emmett–Teller (BET) method, and the mesoporous pore size and pore volume were determined by the Barrett–Joyner–Halenda (BJH) method.

In order to investigate the acidity of the prepared catalyst, ammonia adsorption measurements were performed by the ammonia pulse method. First, 40 mg of sample (particle size, 355–125  $\mu$ m) was sandwiched between quartz wool and filled into a reactor, and the temperature was raised to 600 °C at a heating rate of 10 °C/min under a helium circulation of 30 cc/ min and held for 3 h. Thereafter, the temperature of the catalyst layer was set to 100 °C, and 1.0 cc/pulse ammonia was introduced into the catalyst layer to adsorb ammonia to the catalyst. After the catalyst was held at 100 °C under the He stream, the temperature was raised to 650 °C at a heating rate of 10 °C/min, and ammonia was desorbed. Ammonia gas was detected and quantified using a gas chromatograph with a thermal conductivity detector (TCD) (GC-8A). The measurement conditions were as follows: INJ/IT, 170 °C; COL, 140 °C; ATTN, 16; current, 100 mA; and column flow, 30 cc/min.

In order to measure the amount of coke attached to the catalyst through the reaction, TG-DTA measurement was performed on the catalyst after the reaction. For measurement, the automatic TG-DTA simultaneous measuring device DTG-60AH (Shimadzu Corp.) was used to calculate the amount of coke from the weight difference of the sample before and after measurement. Measurements were carried out under the following conditions: sample amount was 10 mg, ramp speed was 10 °C, measuring temperature was 600 °C, pan used was aluminum, carrier gas was air, and gas flow rate was 100 mL/min.

2.3. Hydrocracking of *n*-Heptadecane Using Pt/ Zeolite-Al<sub>2</sub>O<sub>3</sub> Catalysts. Hydrocracking of *n*-heptadecane was performed using a fixed-bed flow reactor and a stainlesssteel pipe with an inner diameter of 8 mm and an outer diameter of 10 mm (Figure S1). The catalyst bed was placed in the middle of the reactor, and quartz wool (Tosoh Corporation, Fine) was put to both sides of the catalyst of 2 g. The top space of the reactor was filled by quartz sand, and a Pyrex glass tube with an outer diameter of 6 mm was packed at the bottom space. The catalyst included particles with size of 600–355  $\mu$ m (70 wt %) and 355–125  $\mu$ m (30 wt %). The product generated during the reaction was separated by a gasliquid separator, and part of the gas product was collected and exhausted to a draft. After the reaction was performed for the initial 1 h at the same reaction temperature, the liquid product was collected for the next 1 h. The catalyst was reduced at 300  $^{\circ}$ C and H<sub>2</sub> at a rate of 30 mL/min for 3 h before the reaction. The reaction conditions of each catalyst were as follows: 0.5Pt/ Y(100)35A—amount of sample: 2.0 g; reaction temperature: 280, 285, 290, 295, and 300 °C; H<sub>2</sub> pressure: 0.5 MPa; H<sub>2</sub> flow rate: 300 mL/min; weight hourly space velocity (WHSV): 2.3 h<sup>-1</sup>; and 0.5Pt/ZSM(110)35A-amount of sample: 2.0 g; reaction temperature: 250, 255, 260, 265, and 270 °C; H<sub>2</sub> pressure: 0.5 MPa; H<sub>2</sub> flow rate: 300 mL/min; WHSV: 2.3 h<sup>-1</sup>. The gas products of C3–C4 collected at regular intervals were quantitatively analyzed using a gas chromatograph with a flame ionization detector (FID) (GC-FID, GC-2014, Shimadzu Corp.). C1 and C2 were not formed. The composition of the liquid product with C15-C18 was quantitatively analyzed by a GC-FID (GC-2014, Shimadzu Corp.). Liquid products with C5-C14 were also quantitatively analyzed by a GC-FID detector (GC-2010, Shimadzu Corp.) with paraffins, olefins, naphthenes, and aromatics (PONA) solution software (Shimadzu Corp.). Detailed conditions of GC measurement were described in the footnote of Figure S1. Gas chromatography-mass spectrometry (GC-MS) (GC-MS-2010, Shimadzu) was also used to determine isomers of the C17 fraction.



Figure 1. XRD patterns of (a) each fresh catalyst and (b) each used catalyst.

Table 1. Surface Area, Pore Volume, and Average Pore Diameter of Composited Support Catalysts

	BET			ВЈН			
catalyst	$SA^{c}(m^{2}/g)$	$PV^d$ (cm <sup>3</sup> /g)	$PD^{e}(nm)$	$SA^{c}(m^{2}/g)$	$PV^d$ (cm <sup>3</sup> /g)	PD <sup>e</sup> (nm)	
<sup>b</sup> 0.5Pt/Y(100)35A	472	0.64	5.4	243	0.59	3.72	
<sup>a</sup> 0.5Pt/Y(100)35A	401	0.57	5.7	217	0.53	3.72	
<sup>b</sup> 0.5Pt/Z(110)35A	279	0.46	6.5	176	0.40	10.5	
<sup>a</sup> 0.5Pt/Z(110)35A	276	0.44	6.4	175	0.39	10.5	
<sup>a</sup> Used catalysts <sup>b</sup> Fresh cat	olvete <sup>c</sup> Surface area	<sup>d</sup> Pore volume <sup>e</sup> Por	o diamotor				

#### "Used catalysts. "Fresh catalysts. "Surface area. "Pore volume. "Pore diameter

#### 3. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of fresh and used 0.5Pt/ Y(100)35A and 0.5Pt/Z(110)35A catalysts. Both catalysts exhibited signals derived from zeolite and  $\gamma$ -alumina before and after the reaction. Signals derived from Pt did not appear, indicating that Pt would be dispersed in the catalysts.

Table 1 shows the results of  $N_2$  adsorption and desorption measurements before and after the reaction of 0.5Pt/ Y(100)35A and 0.5Pt/Z(110)35A. The differences between pore properties before and after the reaction were not significant, indicating that the structural change due to the reaction would be small. Very small amounts of *n*-heptadecane may remain by adsorption, which may affect the slight decrease in the surface area and pore volume. Further, there may be the formation of a small amount of coke. TG-DTA measurement of used catalysts shown below seems to explain these results.

Figure 2 and Table 2 show results from  $NH_3$ -TPD.  $NH_3$ -TPD curves of 0.5Pt/Y(100)35A and 0.5Pt/Z(110)35A catalysts mainly appeared at the low temperature range from 200 to 350 °C. The shape of the  $NH_3$ -TPD curve for 0.5Pt/



Figure 2. NH<sub>3</sub>-TPD curves of fresh catalysts.

Table 2. Amounts of NH<sub>3</sub> Adsorbed and Desorbed

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Y(100)35A was similar to that for meso-Y zeolite.<sup>30</sup> A relatively higher value was observed for 0.5Pt/Y(100)35A, where part of the Al species in Al<sub>2</sub>O<sub>3</sub> and alumina binder might be combined with the outer surface of zeolite crystals forming new acid sites. A zeolite with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> of 100 or 110 has Al of  $3.3 \times 10^{-4}$  or  $3.0 \times 10^{-4}$  mol/g, respectively. As the zeolite content in the catalyst is 50%, the amounts of Al derived from zeolite were  $1.7 \times 10^{-4}$  and  $1.5 \times 10^{-4}$  mol/g for 0.5Pt/ Y(100)35A and 0.5Pt/Z(110)35A, respectively. Values of total acid sites for these catalysts were  $4.5 \times 10^{-4}$  and  $2.0 \times 10^{-4}$ mol/g, respectively, as shown in Table 2. The value for 0.5Pt/ Z(110)35A is near that of Al derived from zeolite, and the difference might be derived from the adsorption on Pt and  $Al_2O_3$ . The difference for 0.5Pt/Y(100)35A was much higher than that for 0.5Pt/Z(110)35A. As the contents of Pt and Al<sub>2</sub>O<sub>3</sub> were the same, it was assumed that this difference might come from the stability of the zeolite crystal. We have already reported that when commercial Y-zeolite and ZSM-5 were treated with tetraethylorthosilicate and then with a solution of hexamethyldisiloxane and acetic anhydride at 50 °C for 48 h and then at 70 °C for 72 h, mesoporous SiO<sub>2</sub>-surrounded Yzeolite and ZSM-5 hierarchical catalysts could be prepared.<sup>31</sup> In the preparation of these hierarchical catalysts, the extent of decrease in XRD patterns of Y-zeolite crystals was slightly higher than that of ZSM-5 crystals, suggesting that the reactivity of the Y-zeolite surface could be higher than that of ZSM-5.

Figure 3 shows TEM images of 0.5Pt/Y(100)35A and 0.5Pt/Z(110)35A. In both catalyst systems, zeolite crystals



a) Fresh 0.5Pt/Y(100)35A





200nm

c) Fresh 0.5Pt/Z(110)35A

Figure 3. TEM images of fresh and used catalysts.

with 500 nm size were dispersed in the thin layer of  $Al_2O_3$ , and it seems that there would be no significant difference between them before and after the reaction at least in TEM morphology. As the terminal end of a linear hydrocarbon is sufficiently small to enter the pore mouth existing in the surface of catalyst particles, the reaction could proceed. A reactor could often get stopped with the direct use of a fine powder of a single zeolite. Therefore, it seems that the use of  $Al_2O_3$ , which consists of mesopores, could prevent this phenomenon.

Using 0.5Pt/Y(100)35A, hydrocracking of *n*-heptadecane was performed at 280, 285, 290, 295, and 300 °C. Figures 4, S2



Figure 4. Carbon number distribution of products in hydrocracking of n-heptadecane using 0.5Pt/Y(100)35A.

and Table S1 show the carbon number distribution of products in hydrocracking of *n*-heptadecane, PONA distribution, and the conversion, selectivity of products, and aromatic yield, respectively. The conversion was 78% at 280 °C, and it increased with temperature and reached 99% at 295 °C. The selectivity for the jet fuel fraction of C8–C16 was 27% at 280 °C, which increased with increasing temperature and reached 74% at 295 °C. Gas formation was suppressed at all temperatures, and the selectivity for gas products was controlled to as low as 7% even at 295 °C. The selectivity

for isomers of C17 was also suppressed to 8% at 295 °C. Aromatics were not produced at all the temperatures tested. When it is assumed that a carbenium ion might be formed at the carbon from 2 to 16 positions of *n*-heptadecane with the same probability, compounds with C3–C14 were formed at the same molar ratio. In that case, the selectivity (or yield) of the jet fuel fraction of C8–C14 reached 75%. This value was almost the same as C8–C16 of 74% at 295 °C using 0.5Pt/ Y(100)35A, and the yield accounted for 73%. When the product distribution in Figure 4 was seen, the selectivity for C3 was lower, and those for C5–C7 were somewhat lower, suggesting that dimerization of C3 with the C5–C7 fraction could occur to some extent.

Using 0.5Pt/Z(110)35A, hydrocracking of *n*-heptadecane was performed at 250, 255, 260, 265, and 280 °C. Figures 5, S2



Figure 5. Distribution of carbon number for products on hydrocracking of n-heptadecane using 0.5Pt/Z(110)35A.

and Table S2 show the carbon number distribution of products in hydrocracking of *n*-heptadecane, PONA distribution, and the conversion and selectivity of products and aromatic yields, respectively. The conversion extremely increased from 71 to 97% between very small range of 265 and 270 °C. The selectivity for the jet fuel fraction of C8-C16 was 60% at 250 °C, which decreased constantly with increasing temperature, and was 22% at 270 °C. Gas formation increased with temperature and reached 37% at 270 °C. Consistent with the cases of 0.5Pt/Y(100)35A, no aromatics were produced at temperatures used. Temperature control was difficult with the use of ZSM-5 to obtain jet fuel fraction selectively, and it is concluded that ZSM-5 could not be suitable for this reaction. It seems that due to the higher crystallinity, stronger acid sites, and narrower pore mouth of ZSM-5, the control of the jet fuel range in hydrocracking would be difficult.

Hydrocracking of *n*-hexadecane using supported Pt and Pd catalysts in the literature could be compared with our data (Table 3).<sup>5,9-11</sup> In these catalysts, Pt or Pd loading amount was in the range of 0.5-1 wt %. Supports were MCM-41,<sup>5</sup> ZSM-22,<sup>6</sup> heteropolymolybdate/MCM-41 composite,<sup>8</sup>  $\beta$ zeolite,<sup>9</sup> dealuminated HY-zeolite,<sup>10</sup> and SBA-15/ $\beta$ -zeolite composite.<sup>11</sup> Some of these reports dealt with isomerization, and the jet fuel yields were rather low. Two examples of dealuminated HY-zeolite-supported and SBA-15/ $\beta$ -zeolite composite-supported Pt catalysts<sup>10,11</sup> using higher temperature and pressure than ours yielded only 51% of jet fuel fraction because of secondary cracking of primary cracking products which decreases the jet fuel fraction. Our result was the almost ideal jet fuel yield (C8-C14) of 75% by weight, which was obtained by assuming that carbocations from the 2nd to 16th position in *n*-C17 could undergo  $\beta$ -scission at the same probability. In this calculation, hydrocarbons were formed by a

## Table 3. Yields of Jet Fuel Fraction in Literature

catalyst	conditions	conv. (%)	yield of jet fuel (%)	refs
1Pd/MCM-41	<i>n</i> -C16, 340°C, 60 bar H <sub>2</sub> , 10 h <sup>-1</sup> WHSV	50	13 (C8-C14)	5
0.9Pt/H-BEA23	<i>n</i> -C16, 215°C, 20 bar H <sub>2</sub> , 875 kg s mol <sup>-1</sup> W/F	50	41 (C7–C13)	9
1Pt/HY-DA	<i>n</i> -C16, 327.5°C, 2 MPa H <sub>2</sub> , 32 h <sup>-1</sup> WHSV	100	51 (C8-C14)	10
0.5Pt/80AlSBA-15/20BEA	<i>n</i> -C16, 320°C, 5 MPa H <sub>2</sub> , 3.5 h <sup>-1</sup> WSHV	96	51 (C8-C13)	11
Pt/HY(100)	n-C15–n-C18 (biohydrogenated diesel, BHD), 310°C, 450 psig, 1.0 h <sup>-1</sup> LHSV, 30 (mol/mol) H <sub>2</sub> /BHD	90	44 (C8–C14)	24
0.5Pt/Y(100)35A	<i>n</i> -C17, 295°C, 0.5 MPa H <sub>2</sub> , 2.3 h <sup>-1</sup> WHSV	99	73 (C8–C15)	this work
0.5Pt/Z(110)35A	<i>n</i> -C17, 265°C, 0.5 MPa H <sub>2</sub> , 2.3 h <sup>-1</sup> WHSV	71	23 (C8-C15)	this work

same mole number for each fraction from C3 to C14. If a similar calculation was applied for *n*-hexadecane, hydrocarbons from C3 to C13 were given by the same mole number for one carbon number, and therefore the maximum yield of C8–C13 was 72%. Results in literature have not approached this value yet. In the present study, composites supports of Y(100)35A and Z(110)35A were used and included only 50 wt % of zeolite. Therefore, the acidity of zeolite was weakened and the overcracking was inhibited, which seem to be very important for the increase in the yield of jet fuel, middle range of hydrocarbons. The coke formation was also inhibited as shown in Table 4 of TG-DTA results. Further, the size of the

Table 4. TG-DTA Measurement of Pt/zeolite-Al<sub>2</sub>O<sub>3</sub> Catalysts

catalysts	200– 300°C	300– 400°C	400– 500°C	500– 600°C	total (mg) (400–600°C)
0.5Pt/Y(100)35A	0.08	0.05	0.06	0.05	0.24 (0.11)
0.5Pt/Z(110)35A	0.11	0.08	0.11	0.09	0.39 (0.20)

supercage of Y-zeolite is large enough to treat long-chained hydrocarbons and keep them in its inside before cracking, which would inhibit the overcracking of hydrocarbon products.

## 4. CONCLUSIONS

One of the most promising methods to prepare SAF is the hydrocracking of hydrotreated biodiesel fraction C15–C18 obtained from the biomass fat or FT wax. In the present study, Y and ZSM-5 zeolite-Al<sub>2</sub>O<sub>3</sub> composite-supported Pt catalysts were prepared and were tested for hydrocracking of *n*-heptadecane (C17) using a fixed-bed reactor under the conditions of 0.5 MPa H<sub>2</sub> pressure, 300 mL/min H<sub>2</sub> flow rate, 2.3 h<sup>-1</sup> WHSV, and 2 g of catalyst weight. When HY-zeolite (50 wt % SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 100)-Al<sub>2</sub>O<sub>3</sub> (50 wt %) composite-supported Pt (0.5 wt %) catalyst (0.5Pt/Y(100)35A) was used, fine-tuning to the reaction temperature to 295 °C achieved a high selectivity of 74% for the jet fuel fraction of C8–C16 and a high conversion of 99%. In contrast, when 0.5Pt/Z(110)35A was used, the hydrocracking to the C3–C7 fraction could not be suppressed.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c07678.

Conversion and selectivity of products and aromatic yields, reaction device of hydrocracking, and distribution of PONA in products on hydrocracking of *n*-heptadecane (C8-C16) (PDF)

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#### Notes

The authors declare no competing financial interest.

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