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TGA-Based Thermokinetics of High-Viscosity Oil Decomposition in the Presence of Nanocatalysts, Catalytic Additives, and Polymers

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Abstract—The paper provides experimentally determined thermokinetics of the thermal decomposition of high-viscosity oil (HVO) from the Karazhanbas field, the Republic of Kazakhstan, in the presence of a Fe_3O_4 nanocatalyst, catalytic additives (nickel catalytic additives in microspheres prepared from coal ash), and polymers (such as polyethylene glycol and polystyrene) as hydrogen donors. The HVO decomposition thermokinetics (activation energy, pre-exponential factor, and rate constants), depending on the presence of nanocatalysts, catalytic additives, and/or polymers, were estimated by thermogravimetry methods in an inert nitrogen atmosphere. The experimental data (including HVO weight loss and weight loss rate vs. temperature) and the estimated thermokinetics of HVO decomposition can be used to create a database appropriate for mathematical modeling of the processing of HVO and heavy oil residues.

Keywords: high-viscosity oil, thermogravimetry, thermokinetics, polystyrene, polyethylene glycol

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In view of the global slowdown in the growth of conventional hydrocarbon reserves, including conventional crude oil, efforts have been intensified to search for effective methods for the processing of heavy high-viscosity oils (HVO).

High-viscosity oils in the Republic of Kazakhstan (RK) are known to be lean in low-boiling and medium-boiling hydrocarbons and rich in asphaltenes, total sulfur, and heavy metals such as vanadium and nickel. The high content of these metals precludes effective processing of heavy oils using technologies available in the RK due to the rapid and irreversible deactivation of catalysts used on an industrial scale.

One known method to process heavy hydrocarbon feedstocks (which consist of heavy oil residue, high-viscosity oil, residual fuel, and coal) is thermal cracking in the presence of polymeric materials and catalysts. Due to their high hydrogen content (up to 14 wt %), polymers such as polyethylene, polypropylene, polystyrene [1–5] etc. can be used as a source of hydrogen for the hydroconversion [6] and thermal processing [7] of heavy and solid hydrocarbon feedstocks.

Linear polymers are known to improve the performance of co-hydrogenation with vacuum residue [7]. However, there has been very limited public information on the utilization of polymers as hydrogen donors for hydrogenation of heavy oil residues and HVO.

The purpose of this study is to determine the thermokinetic parameters for the decomposition of a HVA/polymer mixture in the presence of a nanocatalyst or a catalytic additive.

EXPERIMENTAL

The high-viscosity oil samples for the study were sourced from the Karazhanbas field, RK. Table 1 presents the physicochemical properties of this HVO. Its molecular weight was measured by cryoscopy.

Table 1. Physicochemical properties of Karazhanbas HVO

Property	Value
Density, kg/m^3	943.1
Kinematic viscosity at 30°C, cSt	539
Molecular weight, g/mol	384
Content, wt %	
Paraffins	1.5
Asphaltenes	4.9
Resins	24.2
Elemental composition, wt %	
C	82.5
H	11.8
N	0.9
S	2.6
O	2.3
Carbon residue, wt %	7.2
HC distillate yield, wt %	
< 200°C	2.6
200–250°C	3.0
250–300°C	6.8
300–350°C	10.1
Metal content, g/t	
Vanadium	320
Nickel	65–70

For the experiments, we used a Fe_3O_4 nanocatalyst 15 nm in diameter [8], as well as NiO/microsphere catalytic additives (nickel salt deposited by wet mixing [9] on the surface of microspheres obtained from the coal ash from the RK). Coal ash microspheres have proven highly efficient in the thermal decomposition of heavy oil residues [10]. The efficiency of nanocatalytic additives such as microspheres and NiO/microspheres in the hydrogenation of a model mixture of anthracene and phenanthrene is also known [11].

Synthetic polymers have been widely used as hydrogen donors in coal liquefaction to coal oil [12, 13]. However, to the authors' best knowledge, there are no available references on the use of polyethylene glycol (PEG) and polystyrene as additives for HVO thermal decomposition.

We examined the following polymers: PEG (M = 6000 g/mol, CP grade) and polystyrene (M = 300 000 g/mol, CP grade), both manufactured in Norchem's Synthanol Plant, Russia.

Thermal degradation of polystyrene leads to the formation of highly reactive hydrogen atoms [14], which likely stabilize free radicals resulting from HVO thermal degradation.

PEG is known to be used as a phase transition catalyst to accelerate a reaction at the solid–liquid interface [15, 16]. PEG's donor/acceptor properties can be controlled by replacing OH groups, e.g., by amino groups or metal oxides [17].

The individual chemical composition of the microsphere used as a catalytic additive and as a support for nickel salt solutions was measured as per GOST 10538-87 (%): SiO_2 (56.92), Al_2O_3 (35.96), Fe_2O_3 (2.97), CaO (0.78), MgO (1.25), K_2O (0.83), Na_2O (0.92), P_2O_5 (0.09), MnO (0.04), TiO_2 (1.72).

To prevent any diffusion effects and ensure homogeneity for the process when preparing a sample for thermogravimetry, 4 g of Al_2O_3 was placed in a crucible and calcined in a muffle furnace at 600°C for 2 h. After the calcination, the sample was dried in a desiccator.

0.04 g of a polymer was added to 0.2 g of HVO, then 1% (by weight of HVO) of the nanocatalyst or catalytic additive was introduced as an optimal amount for the destructive hydrogenation of the feedstock [8], 3.0 g of dried Al_2O_3 was added, and the mixture was stirred to homogeneity.

The initial high-viscosity oil and the HVO/nanocatalyst/catalytic-additive/polymer mixtures were subjected to thermal analysis using LABSYS™ EVO (TG/DTA/DSC/1600°C) instruments (Setaram, France). A 17 mg sample (weighing accuracy ±0.01%) was placed into a 2 mL alumina crucible with a constant heating rate of 10 K/min from 298 to 783 K in a nitrogen medium. The gas flow rate was 30 mL/min.

There are a number of approaches to examine the thermal degradation kinetics based on thermogravimetric analysis (TGA). The best-developed approach is applicable to a single-stage design or to processes that consist of several stages each occurring within a distinct temperature range and which, thus, can readily be subdivided into gross processes. Such a process is generally assumed to be described by the Arrhenius equation with respect to the rate of reaction of order *x*:

$$\frac{dm}{d\tau} = -k_0 e^{-E/RT} m^x,$$

where m is the weight of non-volatile matter in the sample (mg) at time τ (min); E is the activation energy (kJ/mol); k_0 is the pre-exponential factor (min^{-1}); R is the universal gas constant (kJ/mol); T is the absolute temperature, K; and x is the order of reaction.

Importantly, in this case one should focus not on the kinetic constants of specific reactions of individual substances, but rather on the total thermal decomposition parameters that describe the variations in the total weight of a sample as a temperature function over the course of heating at a certain rate. For this reason, it is often impossible to use the values of k_0, E, and x estimated under specific thermal degradation conditions to describe the thermal decomposition of the same substance under other conditions (e.g., a different heating rate).

A book by Gyulmaliev [18] and an article by Papkov and Slonimskii [19] described a method to determine the kinetics of thermal decomposition of coal based on relevant TGA data. In particular, having used one TGA curve point in which the degradation rate reaches its maximum, they have transferred the results to the entire curve. However, such an approach is not always sufficiently grounded. Moreover, this method appears to be unacceptable for an insufficiently definite system with three unknowns. For example, the procedure begins by estimating the order of the degradation reaction based on the mass conversion degree of the initial substance in the inflection point. Then the activation energy and the pre-exponential factor of the process are derived from the reaction order, conversion degree, and temperature at the same point. Obviously, with such an approach the estimation errors rapidly build up for each subsequent parameter. The precision of the system can be improved by taking $x = 1$. This is often justified for degradation processes. Moreover, the choice of the first order has another advantage: in this case the dimension of k_0 includes only time, while the measurement unit of the quantity of substance does not matter at all.

More promising is a method for determining the kinetic parameters of the thermal degradation of carbon-containing substances which describes the entire section of the TGA curve relating to a single gross stage. This method was formulated and tested in studies by Bukharkina et al. [20] and Lyrshchikov et al. [21].

In the current study, the thermal decomposition kinetics (rate constant, activation energy, and pre-exponential factor) of HVO and of a HVO/catalyst/polymer mixture were estimated using both the method proposed by T. Bukharkina and the method suggested by A. Gyulmaliev.

RESULTS AND DISCUSSION

The TGA curves of weight loss and weight loss rate in an inert atmosphere for HVO in the presence of nanocatalysts, catalytic additives, and hydrogen donors are demonstrated in Figs. 1 and 2.

Figure 1 shows that HVO weight losses begin at 471 K, while the addition of various catalytic additives and polymers increases the HVO thermal decomposition temperature by about 50 K. The weight compositions of the HVO/polymer/catalyst mixtures (samples) are listed below:

Sample 1: HVO with no additions

Sample 2: HVO in the presence of polystyrene—0.833:0.167

Sample 3: HVO in the presence of polystyrene with Fe_3O_4 nanocatalyst—0.826:0.165:0.008

Sample 4: HVO in the presence of PEG—0.833:0.167

Sample 5: HVO in presence of PEG with NiO/microsphere—0.826:0.165:0.008

Sample 6: HVO in presence of PEG with microsphere—0.826:0.165:0.008

A comparison of the TGA weight loss curves for the mixtures of Sample 2 (HVO/polystyrene, Fig. 1b) and Sample 4 (HVO/PEG, Fig. 1d) within the temperature range of about 505 K to about 730 K indicates a weight loss of about 70% for Sample 2 and a weight loss of about 60% for Sample 4.

Figure 2 illustrates the weight loss rates during the thermal decomposition of HVO in the presence of nanocatalysts, polymers, and/or additives. The highest weight loss rate was observed in the presence of polystyrene with Fe_3O_4, while the lowest rate was in the presence of PEG with NiO/microsphere.

For Sample 2 (HVO/polystyrene), the maximum weight loss rate is about 0.33 mg/min at 730 K; for Sample 4 (HVO/PEG), the maximum weight loss rate (about 0.45 mg/min) manifests itself at 750 K. Adding Fe_3O_4 to the HVO/polystyrene mixture boosts the weight loss rate to about 0.45 mg/min. The addition of microspheres and NiO/microspheres to the HVO/PEG mixture results in a maximum weight loss rate of about 0.20–0.25 mg/min at 700–750 K.

The highest weight loss rate resulting from thermal decomposition is observed in the HVO/polystyrene/Fe_3O_4 mixture, while the lowest value corresponds to the HVO/PEG/NiO/microsphere mixture (Fig. 2).

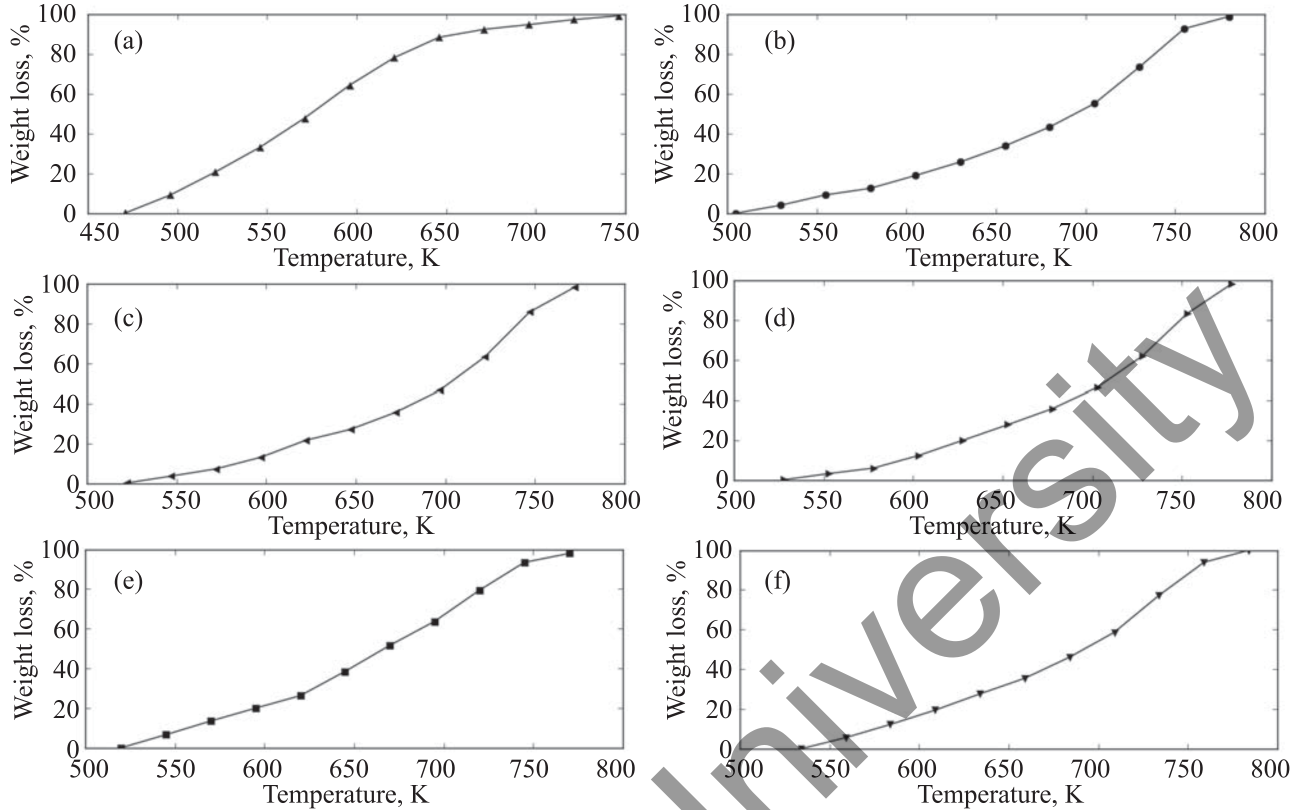

Fig. 1. TGA weight loss curves for HVO samples in the presence of nanocatalysts, catalytic additives, and/or polymers: (a) Sample 1, HVO; (b) Sample 2, HVO/polystyrene; (c) Sample 3, HVO/polystyrene/Fe_3O_4; (d) Sample 4, HVO/PEG; (e) Sample 5, HVO/PEG/NiO/microsphere; (f) Sample 6, HVO/PEG/microsphere.

The weight loss rate variation with temperature appears to be associated with the presence of a thermoplastic phase and an elastic phase in the system, each affecting the HVO thermal degradation depending on the type of polymer and catalyst involved.

The TGA data are linearized in coordinates as follows:

$$\ln[r_i / (m_{i\,\max} - m_{i\,\min})] — f\left(\frac{1}{T}\right),$$

where r_i is the rate of the ith stage of the first-order reaction (mg/min); m_i is the current weight of volatiles released in the ith stage (mg); and T is the absolute temperature (K) (Fig. 3). From the straight-line equation, the activation energy and the pre-exponential factor were derived.

The thermokinetic parameters (pre-exponential factor k_0 and activation energy E) of the decomposition of high-viscosity oil and HVO/nanocatalyst/catalytic-additive/polymer mixtures estimated in accordance with the TGA method described in reference [20] are summarized in Table 2.

Table 2 shows that the highest activation energy and pre-exponential factor of HVO decomposition (41.47 kJ/mol and 8.6×10^3 s^{-1}, respectively) correspond to the HVO/PEG/microsphere case, while the lowest activation energy and pre-exponential factor are, respectively, 15.9 kJ/mol in the presence of polystyrene and 5.74 s^{-1} in the presence of PEG. The highest weight loss rate—observed in the 697–722 K range for the HVO/polystyrene/Fe_3O_4 sample (Fig. 2)—concurs with an activation energy of 22.3 kJ/mol. For the HVO/PEG/NiO/microsphere mixture, with its low weight loss rate within the temperature range of 695–720 K, the activation energy is 30.74 kJ/mol.

It should be noted that the thermokinetics estimation method using the entire curve shows a very weak correlation between the activation energy and the thermodegradation rate for the mixtures under study.

Table 2 further demonstrates that the activation energy for the decomposition of the initial HVO is 34.5 kJ/mol, while the same parameter for the HVO/PEG/microsphere mixture reaches 41.47 kJ/mol. In contrast,

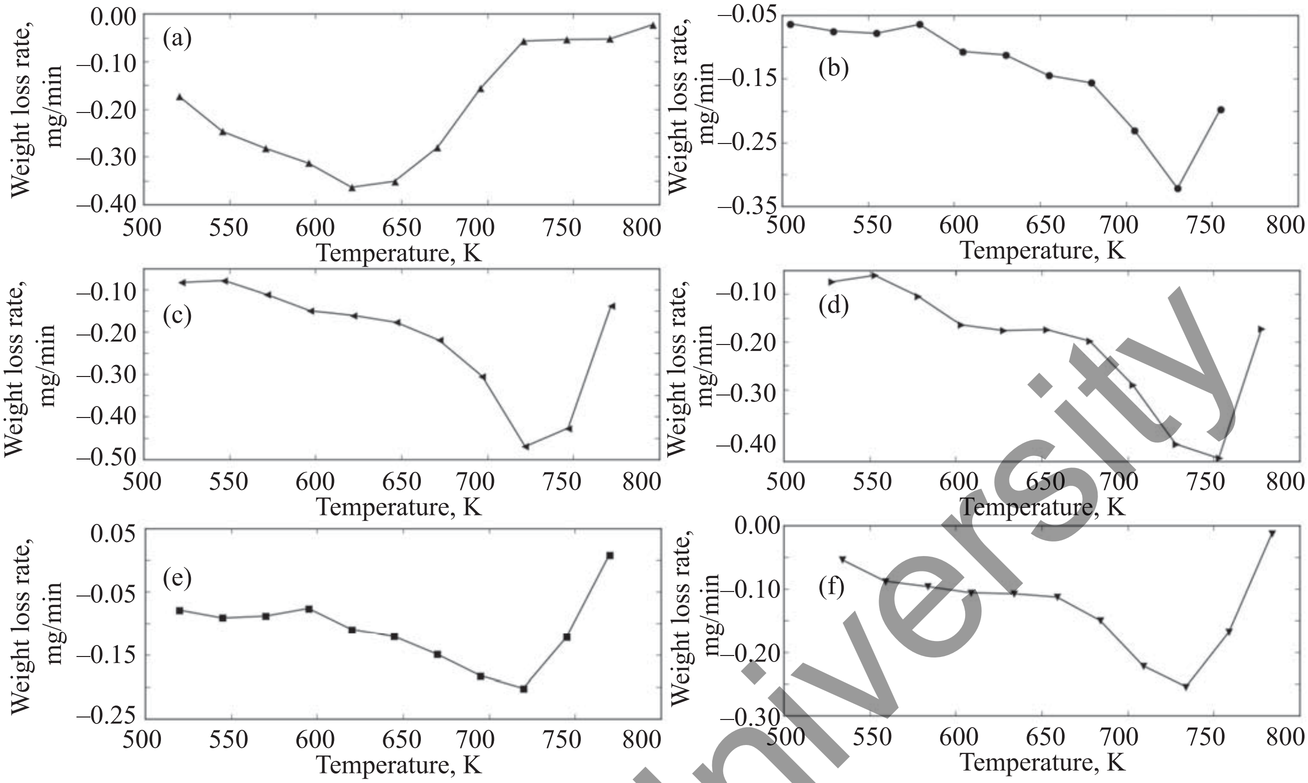

Fig. 2. TGA weight loss rate curves for HVO samples in the presence of nanocatalysts, catalytic additives, and/or polymers: (a) Sample 1, HVO; (b) Sample 2, HVO/polystyrene; (c) Sample 3, HVO/polystyrene/Fe_3O_4; (d) Sample 4, HVO/PEG; (e) Sample 5, HVO/PEG/NiO/microsphere; (f) Sample 6, HVO/PEG/microsphere.

adding polystyrene as a hydrogen donor decreases the activation energy to 15.9 kJ/mol.

It is known that, in thermal processes, tertiary hydrogen atoms in polystyrene chains are highly reactive with respect to free radicals [14], while PEG can act as a phase transition catalyst [16].

The use of non-isothermal kinetics and dynamic TGA methods to identify the kinetic patterns of the degradation of heavy hydrocarbon feedstocks is described in published reports [22]. Specifically, these methods enable researchers to estimate the activation energy, enthalpy, and entropy of the thermodegradation of heavy hydrocarbon feedstocks based on relevant TGA curves. The kinetics (i.e., rate constant *k* and activation energy *E*) of the thermal decomposition of the high-viscosity oil and the HVO/nanocatalyst/catalytic-additive/polymer mixtures estimated by the TGA method described in reference [18] are summarized in Table 3.

Table 3 clearly shows that the addition of hydrogen donors, nanocatalysts, and catalytic additives to initial HVO significantly decreases the activation energy as well as the decomposition temperature. During the HVO thermal decomposition, the rate constant is 3.56×10^{-2} min^{-1}, while it drops to the lowest level in the HVO/PEG case.

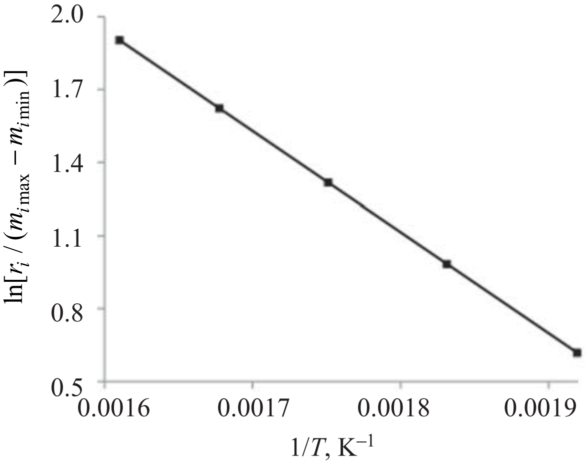

Fig. 3. Linearization of HVO thermal degradation rate as a function of temperature.

Table 2. Thermokinetics of thermal decomposition of high-viscosity oil and HVO/nanocatalyst/catalytic-additive/polymer mixtures (acc. to Bukharkina [20])

Sample no.	Description	Temperature range, K	k_0, s^{-1}	E, kJ/mol
1	High-viscosity oil	471–621	5.4×10^3	34.50
2	HVO/polystyrene	505–730	78.7	15.90
3	HVO/polystyrene/Fe_3O_4	522–722	202.1	22.30
4	HVO/PEG	528–753	5.74	30.30
5	HVO/PEG/NiO/microsphere	520–745	1.24×10^3	30.74
6	HVO/PEG/microsphere	534–759	8.6×10^3	41.47

Table 3. Thermokinetics of thermal decomposition of high-viscosity oil and HVO/nanocatalyst/catalytic-additive/polymer mixtures (acc. to Gyulmaliev [18])

Sample no.	Description	Temperature range, K	k_0, s^{-1}	E, kJ/mol
1	High-viscosity oil	471–621	3.56	161.88
2	HVO/polystyrene	505–730	1.07	45.96
3	HVO/polystyrene/Fe_3O_4	522–722	0.74	26.34
4	HVO/PEG	528–753	0.67	21.92
5	HVO/PEG/NiO/microsphere	520–745	1.03	36.54
6	HVO/PEG/microsphere	534–759	1.00	37.32

The thermal decomposition activation energies presented in Table 3 differ from those indicated for the same samples in Table 2. This discrepancy is likely explained by the fact that Gyulmaliev [18] uses the inflection point in a weight loss vs. temperature curve, whereas Bukharkina [20] considers HVO thermodegradation rate as a function of temperature at each point.

In summary, the TGA method enables researchers to examine various effects on the thermal decomposition of high-viscosity oil. Different catalysts, catalytic additives, and/or polymers are added to initial HVO to change the rate of thermal decomposition of the heavy hydrocarbon feedstock.

The methods presented in the studies by A. Gyulmaliev and T. Bukharkina are effective for estimating the thermal decomposition kinetics of initial high-viscosity oils and HVO-based mixtures. The method described by Gyulmaliev [18] is the most acceptable for determining the thermal decomposition rate of heavy hydrocarbon feedstocks. This method consists of using one inflection point in the TGA curve to estimate the HVO degradation thermokinetics (including the reaction order, rate constant, pre-exponential factor, and activation energy) with high accuracy. In the method described by Bukharkina [20], the TGA curve (sample weight vs. temperature at specific heating rate) represents a slope curve at each point, which serves to determine the degradation rate at a specific temperature and at a specific decomposition degree. The disadvantages of the method include a considerable estimate error (due to the difficulty of proper tangent slope determination) and the high labor intensity of the estimation.

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CONFLICT OF INTEREST

The authors declare no conflict of interest requiring disclosure in this article.

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