

*Research article***Bio-oil upgrading by cracking in two-stage heated reactors**Lihao Chen^{1,*} and Kunio Yoshikawa²

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Abstract: The objective of this research is to explore the possibility to upgrade gasified bio-oil in bench-scale fixed bed reactors with two heating units using the cracking method. The bio-oil is derived from Japanese cedars which are widely distributed in Japan. The catalyst is HZSM-5 zeolite, which is commonly used in bio-oil upgrading. The result showed that by using two heating units, even without catalyst, the upgrading was achieved as well. The catalytic cracking promoted the deoxygenation rate and further improved the quality of the upgraded oil compared with the non-catalytic cracking case. By separating two heating units with different operating condition, the catalytic effect and the deactivation of the catalyst was clarified. The raw bio-oil and the upgraded oil were characterized by measuring their element content, water content and the chemical composition of its organic fraction.

Keyword: cracking; bio-oil upgrading; zeolite catalyst; fixed bed; two-stage reactors

1. Introduction

Biomass sources are widely recognized as a potential future solution to the energy problems worldwide [1,2]. It provides the only source of renewable liquid fuel [3]. Bio-oil, a liquid product of biomass pyrolysis, is a complex mixture of several hundreds of organic compounds that exhibit a wide range of chemical functionality [4]. Characteristic examples of the bio-oil compounds are single ring containing compounds and polycyclic aromatic compounds [5].

The bio-oil applied in this study is produced from the cedar pollard, a kind of waste biomass. In order to be used as a liquid fuel, two main problems needs to be solved: high viscosity and high

oxygen content [6,7]. These two problems lead to undesirable combustion phenomenon such as insufficient energy density, incomplete combustion and blockage [8].

To solve such problems, the main upgrading methods include the hydrogenation [9,10], the cracking [11,12], the solvent addition [13], the steam reforming [14,15] and the emulsification [16,17]. However, none of these bio-oil upgrading technologies have been widely commercialized due to high cost and low fuel efficiency [18]. The cracking method is highly feasible because it can be realized at the atmospheric pressure and no additives are required [19,20].

The popular cracking methods are fixed bed cracking, moving bed cracking and fluidized bed cracking [21,22]. The fixed bed cracking is chosen in this study for its simple equipment requirements.

Many types of catalysts have been studied in the literatures in order to investigate how far the catalyst can modify the bio-oil composition and the bio-oil quality. Most of these studies are focusing on the comparison of catalysts but not on the mechanism of catalysts. The control test without catalyst is considered unnecessary in these studies [23–29].

However, in this paper, the effect of the commonly used catalyst HZSM-5 was discussed focusing on the comparison with the non-catalytic cracking. Most studies on the catalytic cracking of bio-oil are using only one heating reactor, where all components of bio-oil are in contact with the catalyst, including the components that tend to deactivate the catalyst. In this paper, two heating units were employed so that the raw bio-oil was separated in the first heating unit and the cracking was done in the second heating unit. The components liable to deactivate the catalyst can be identified by changing the temperature in the first heating unit. In this way, the catalyst deactivation caused by different components were analyzed simultaneously, instead of treating the bio-oil as a whole [30,24], using model components separately [20] or analyzing the deactivated catalyst after the reaction [31].

Some researches reported that bio-oil component separation is difficult under the atmospheric pressure and side reactions tend to occur due to the poor heat stability of bio-oil [32,33]. But in this paper, side reactions did not significantly affect the experimental results by employing the two-stage heated reactors. Indeed, it is difficult to separate all components in bio-oil individually, but the components can be divided into 4 classes according to the chemical analysis, which was sufficient to explain the reaction mechanism of the deactivation. Different from the one heating unit process which is commonly used, the components in the upgraded bio-oil can be divided into 4 classes of organic components clearly by employing two heating units. By analyzing the reaction trend of these four classes of bio-oil components, the deactivation principle of the catalyst can be discussed without using model compounds. Previous studies generally considered that high molecular weight aromatic and aliphatic compounds are important reasons for deactivation of catalysts [1,34], but in this research, the effects of phenols and naphthalenes on the catalyst were investigated to show the importance of their effects.

2. Materials and methods

2.1. Materials

2.1.1. Bio-oil

The bio-oil was produced from the pyrolysis of Japanese cedar. The pyrolysis gas produced in

an updraft gasifier passed through a cooler to remove water and heavy tar and then was introduced to a centrifuge separator to recover the bio-oil [35].

The elemental content and properties of the bio-oil are listed in Table 1.

Table 1. The element analysis and properties of the raw bio-oil.

Element and properties of bio-oil	
C (%)	57.5
H (%)	7.0
N (%)	0.0
O (%)	35.5
S (mg/kg)	0.0
H ₂ O (%)	8.3
Ash (%)	0.0
Density (g/cm ³)	1.14
HHV (MJ/kg)	23.1
Cetane index	<20
Kinetic viscosity (mm ² /s @ 50 °C)	12.7

*Cetane index of bio-oil was unable to measure accurately for its high density.

2.1.2. Catalytic materials

The HZSM-5 catalyst used in the experiment was provided by Tosoh corporation. Prior to the experiments, the catalytic materials were calcined at 500 °C for 3 h and stored in a desiccator. Its properties are listed in Table 2.

Table 2. Properties of the catalyst.

Properties of the catalyst	
Pore size (Å)	5.8
SiO ₂ /Al ₂ O ₃ (mol/mol)	40
Specific surface area (m ² /g)	330
Crystal size (µm)	2 × 4
Particle size (µm)	10
NH ₃ -TPD (mmol/g)	1.3

2.2. Experimental set-up

The schematic diagram of the experimental set-up is shown in Figure 1. The raw bio-oil was firstly introduced to the first heating unit and then gasified into the second heating unit, with or without packing of the catalyst. As a carrier gas, N₂ gas was fed at the flow rate of 10 mL/min from the top of the first heating unit for the continuous withdrawal of the products and the maintenance of the inert atmosphere during cracking. The product flowing out from the bottom of the second heating unit was in gaseous form, and was condensed in a glass receiver submerged in an ice-water bath. Non-condensable gases were collected in a gas bag. A filter was placed between the ice-water bath

receiver and the gas bag for recovering condensable vapor which might leak from the condenser.

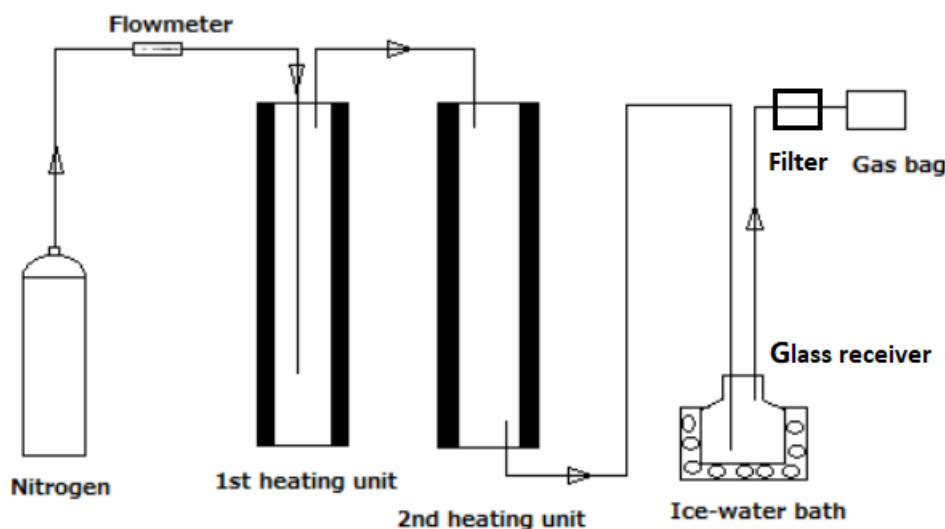


Figure 1. Schematic diagram of the experimental set-up.

2.3. Experimental procedure and product collection

Initially, the second heating unit was filled with 10 g catalyst (catalytic cracking) or no catalyst (non-catalytic cracking), while the first heating unit was filled with 30 g of the raw bio-oil. The first heating unit was heated to a specified temperature. The first heating unit was heated externally to the different set temperature in different heating time, after the second heating unit was heated to 500 °C for 60 minutes. Every operation lasted one hour to ensure the reaction is complete. The operating condition was listed in Table 3.

Table 3. Operating conditions.

Operation Condition	Set temperature of the 1 st heating unit	Heating time
Partial Gasification (PGF)	510 °C	15 min
Further Gasification (FGF)	550 °C	18 min
Complete Gasification (CGF)	600 °C	21 min

As show in Table 3, under the PGF operation condition, both the heated temperature and heating time was less than the FGF and CGF condition. The liquid products were collected and quantitatively measured in the pre-weighted glass receiver. When changing the set temperature higher than 600 °C, no more liquid was collected than CGF condition. Therefore, all volatile components are considered to be gasified under the CGF condition. The non-condensable gas products were collected and measured by difference. The amount of the residue left in the first heating unit was measured by weighing the first heating unit before and after the experiment. The solid products consisted of the coke left in the first heating unit and the coke on the catalyst in the second unit. The amount of condensable vapors recovered in the filter was also weighed by difference and the weight was added to the liquid products yield.

2.4. Analysis methods

The following characteristics were determined: the elemental analysis of C, H, O, N, the moisture content, the ash content, the density, the high heating value (HHV), the cetane index, the kinetic viscosity and the chemical composition.

The ash content and the elemental analysis of C, H, N were determined by JM10 at 950 °C. The elemental analysis of O was determined by Vario micro cube at 1150 °C. The moisture content was measured using Karl Fischer method in accordance with the standards JIS K 2275. HHV was determined in accordance with the standards JIS K 2279. The kinetic viscosity was measured by the ostwald viscometer at 40 °C. The cetane index was calculated in accordance with the standards JIS K 2280-5.

GC-MS is the technique used in the analyses of the product oil composition. A Rxi®-5Sil MS Column was used in the GC and helium was selected as the carrier gas. The oven heating profile was set at an increase of 5 °C/min from 30 to 280 °C.

3. Results and discussion

3.1. Effect of catalyst

In order to investigate the effect of the zeolite catalyst, the cracking with catalyst in the second heating unit was compared with the non-catalytic cracking. In each run, after the second heating unit was heated to 500 °C and kept for 60 min, the first heating unit was heated under the CGF condition and kept for 1 h when no more liquid or gas product could be observed, the yield was weighed and the data was listed in the Table 4.

Table 4. Product yield distribution by weight.

	Liquid	solid	gas
With catalyst	61.3% (water:organic = 16.6:44.7)	19.8%	18.8%
Without catalyst	75.7% (water:organic = 16.8:58.9)	18.3%	14.4%

As shown in Table 4, the gas product from the non-catalyst run was less than the one from the catalyst run, while the liquid product was more.

The upgraded oil in the liquid product was the target in this experiment. The collected liquid product was divided into two layers: the water layer and the organic layer. The element analysis data of the two layers are listed in Table 5.

Table 5. Element analysis of the liquid product.

Element content by weight	Without catalyst		With catalyst	
	Water layer	Organic layer	Water layer	Organic layer
C (%)	21.85	67.91	10.11	73.47
H (%)	9.35	7.83	9.73	7.22
O (%)	68.70	24.07	79.93	19.03

Obviously, some organic matter is soluble in the water layer. That is why C element was also detected in the water layer.

Though in the non-catalytic cracking, the organic liquid product was more than that in the catalytic cracking, the C content was lower and the O content was higher, which means that the heating value of the organic liquid product was lower than the catalytic cracked bio-oil.

Compared with the raw bio-oil properties listed in Table 1, the C content increased by 10% and the O content decreased by 11% in the non-catalytic cracking, while the C content increased by 16% and the O content decreased by 16% in the case of the catalytic cracking. The cracking was achieved without the catalyst, while the zeolite promoted the rate of deoxygenation by 50%.

The possible reason for this promotion was the adsorption and the acidic sites of the zeolite. The adsorption on the surface of the zeolite extended the cracking reaction time of oxygen-containing molecules and the acidic sites contributed to enhance the deoxygenation reaction [36,37]. Other physical properties of the raw bio-oil and the organic liquid products are listed in Table 6.

Table 6. Physical properties comparison of the organic liquid and the raw bio-oil.

	Bio-oil	Organic liquid from catalytic cracking	Organic liquid from non-catalyst cracking
Density (g/cm ³)	1.14	1.02	1.03
Kinetic viscosity (mm ² /s@50 °C)	12.7	4.72	4.85
Water content (%)	8.3	8.0	8.2
Cetane index	<20	39.76	38.18
HHV (MJ/kg)	23.1	31.8	29.9

Significant improvement in physical properties was observed after the cracking regardless of the usage of the catalyst. A further improvement was obtained by using the catalyst.

In order to analyze the phenomenon in more details, GC-MS was employed to identify the chemical compositions of the raw bio-oil and the organic liquid. The result of the raw bio-oil is shown in Figure 2.

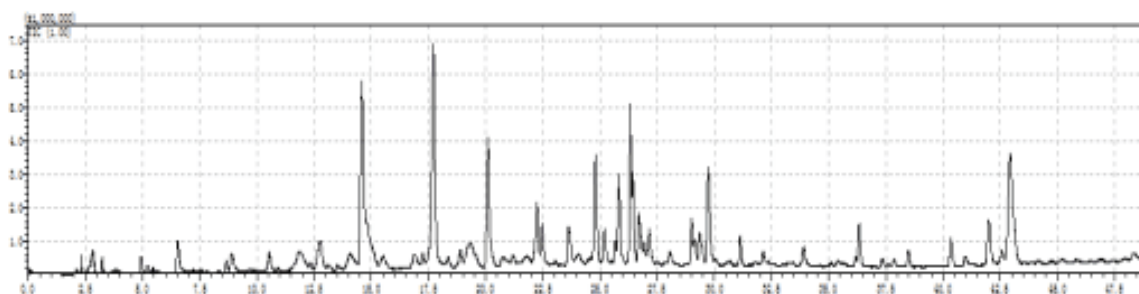


Figure 2. Ion current of the raw bio-oil.

Though hundreds of organics was detected, if picking out the highest 20 peaks, the area of these 20 peaks accounted for 90% of the total area. These 20 organics were listed in Table 7.

Table 7. The main chemical compositions of the raw bio-oil.

Name	Retention time (min)	Area (%)
1-Hydroxy-2-butanone	4.9	1.96
Propanal	5.2	1.26
3,5-Dimethylpyrazole	6.5	1.98
2(5H)-Furanone	8.9	2.36
1,2-Cyclopentanedione, 3-methyl-	12.7	3.90
Phenol, 2-methoxy-	14.6	18.09
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	15.5	1.37
Phenol, 2,4-dimethyl-	16.9	1.55
Creosol	17.7	17.07
Phenol, 4-ethyl-2-methoxy-	20.1	12.98
Phenol, 2-methoxy-3-(2-propenyl)-	22.2	2.31
Phenol, 2-methoxy-4-propyl-	22.5	4.51
trans-Isoeugenol	24.8	5.93
Naphthalene, 1,2,4a,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-	25.8	1.98
Naphthalene, 1,2,4a,5,8,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)- [1S-(1.alpha.,4a.beta.,8a.alpha.)]-	26.3	3.70
Di-epi-.alpha.-cedrene-(I)	29.0	1.44
2-Naphthalenemethanol, decahydro-.alpha.,.alpha.,4a-trimethyl-8-methylene- [2R-(2.alpha.,4a.alpha.,8a.beta.)]-	29.7	2.35
Kaur-15-ene, (5.alpha.,9.alpha.,10.beta.)-	36.3	1.10
Naphthalene, decahydro-1,1,4a-trimethyl-6-methylene-5-(3-methyl-2,4-pentadienyl)- [4aS-(4a.alpha.,5.alpha.,8a.beta.)]-	42.0	1.05
Ferruginol	42.9	2.54

The main components could be divided into 4 classes. The first one is oxygen-containing small molecules with the retention time from 2.5 to 10 min, the main components of which are kinds of ketone, furan and imidazole. The second class is phenols with the retention time of 10 to 25 min, whose main components are guaiacol and its homologues. The third class with the retention time from 25 to 30 min are naphthalenes, which mainly contained naphthalene and naphthol. The fourth one was the materials whose retention time were later than 30 min, mainly containing long-chain aliphatic macromolecular and polycyclic macromolecular structural substances. The area proportions of these four classes are listed in Table 8.

Table 8. Component classification of bio-oil.

	Small molecule	Phenols	Naphthalenes	Macromolecule
Range of retention time (min)	2.5–10	10–25	25–30	>30
Area (%)	8.2%	74.0%	10.8%	7.0%

Figure 3 showed the GC-MS result of the organic liquid products. Two high peaks came out at

the retention time of 5.1 min and 7.8 min after cracking. According to the data base, these two were toluene and xylene, which were most likely the product of the phenolic deoxygenation.

In the catalytic cracking, the phenols peak and the naphthalenes peak decreased more evidently than the non-catalytic cracking, along with more product of toluene and xylene than the non-catalytic cracking. Therefore, more phenolic deoxygenation happened when catalyst was used for cracking. Considering the high thermal stability of benzene ring and naphthalenic ring [38,39], the decrease of naphthalenes shall be interpreted as coking on the catalyst.

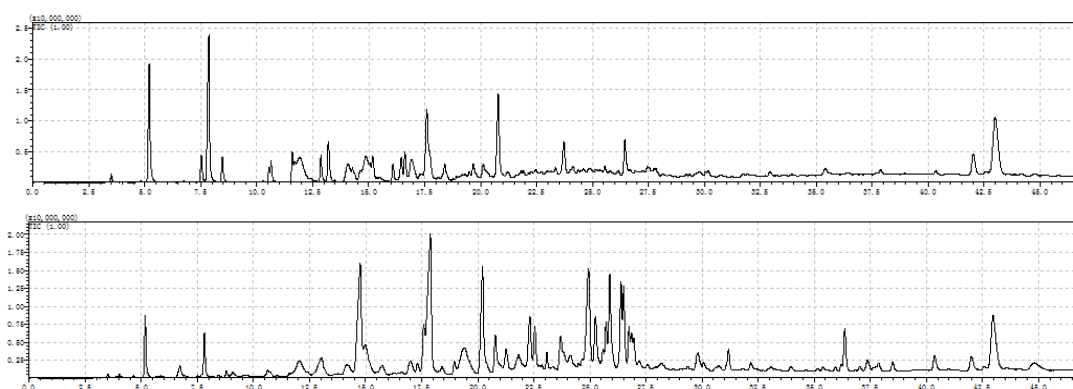


Figure 3. Ion current of the organic liquid of catalytic cracking (above) and non-catalytic cracking (below).

In summary of the above data, the most likely reactions in the second heater unit are the phenolic deoxygenation and the naphthalene coking on the catalyst. In the non-catalytic cracking, the phenols and naphthalenes were directly condensed in the ice-water bath receiver without contact with the catalyst. In order to verify this speculation, different temperatures in the first heating unit were tested in the following section.

3.2. Catalytic test at different temperatures in the first heating unit

In order to confirm the reaction of the 4 component classes, all 3 types of operation condition in Table 3 were tested. At each separation temperature, the experiments were repeated three times without changing the catalyst in the second heating unit, but replacing the residue in the first unit with new bio-oil. The yield was listed in Table 9.

Although the area percentage does not mean the actual content, the data as a reference can be used to summarize the reaction trend.

In the first run at each temperature, the yield of small molecules were higher than the second and the third runs. The yield of phenols in the first run was lower than in the second and the third runs under the PGF and FGF condition. It can be concluded that at the first run of each temperature, the catalyst has the highest activity of converting phenols to toluene and xylene. When the catalyst was reused without regeneration, the activity decreased and more phenols were collected in the condenser than in the first run.

Under the PGF condition, the distilled ingredients from the first heating unit were mainly the small molecule components including oxygen-containing heterocyclic compounds, ketones and

benzenes. From the first run to the third run, the yield of each class did not change significantly, which shows that the deactivation was not serious. Small molecule components was not the main reason for the catalyst deactivation.

Table 9. The area percentage in GC-MS of 4 component classes in the organic liquid at different temperatures in the first heating unit.

Main Ingredients	1st Class Small molecules*	2nd class Phenols	3rd class Naphthalenes	4th class Macromolecules
PGF				
First run	52.0%	40.0%	8.0%	0.0%
Second run	44.8%	43.9%	10.8%	0.0%
Third run	48%	41%	7%	0.5%
FGF				
First run	49.2%	45.0%	5.8%	0.0%
Second run	33.7%	57.3%	9.0%	0.0%
Third run	37.0%	55.5%	7.6%	0.02%
CGF				
First run	34.8%	50.2%	13.6%	1.4%
Second run	18.1%	40.4%	33.4%	7.1%
Third run	11.5%	47.1%	33.1%	8.3%

*The main ingredients of “small molecules” were toluene and xylene.

Under the FGF condition, more phenols were distilled from the first heating unit. That is why the yield of phenols was higher than the one under the PGF condition. After the first run under the PGF condition, a significant decrease of the small molecule components was observed, accompanied by the increase in the yield of phenols. The yields of naphthalene and macromolecules under the FGF condition were in low level similar as in the case of PGF condition. This proved that phenols were important cause of the catalyst deactivation.

When the separation temperature in the first unit came to CGF runs, a big amount of naphthalenes and macromolecules are distilled from the first heating unit. A serious decline happened in the yield percentage of the small molecules from the first run to the second run. A further decline was observed at the third run. It clearly showed that naphthalenes and macromolecules coked on the catalyst, resulting in a serious catalyst inactivation.

Moreover, it should not be considered that the naphthalenes and macromolecules collected in the ice-water bath came from distillation only. Part of them should be the product of the polymerization reaction in the heating process.

Small molecules, whose main component was toluene and xylene, did not contain oxygen. This class of product should be the target product because of the higher heating value. A low separation temperature and shorter heating time should be used to avoid the contact of naphthalenes and macromolecules with catalyst.

3.3. Yield and energy analysis

The yield of the product from the first run in each temperature was listed in Table 10. All feedstocks were converted to water, liquid, coke and gas. The residue referred to the coke in the first heating unit and the increased weight after the cracking tests.

Table 10. The product yield in the weight percentage (%).

	Water	Oil	Gas	Residue
CGF run	16.6	44.7	18.8	19.8
FGF run	14.1	41.2	17.2	27.0
PGF run	11.8	35.1	12.1	40.0

The oil product under PGF operation performed the lowest oxygen content, while that from CDF run performed the highest yield. The comparison of these two product were listed in Table 11.

Table 11. Comparison of product oil and raw bio-oil.

	Bio-oil	Product oil from 300 °C run	Product oil from 130 °C run
C (%)	57.5	73.5	72.3
H (%)	7.0	7.2	11.8
N (%)	0	0	0
O (%)	35.5	19.0	15.9
HHV (MJ/kg)	23.1	31.8	38.6
Yield (%)	-	44.7	35.1
Heat inputs (kJ/g)	-	18.2	16.5
Energy recovery (%)	-	34.3	34.3

The heat inputs referred to the heat put into the reactor for average 1g bio-oil. The recovery rate of the energy was calculated with the Eq 1:

$$\text{Energy recovery} = \frac{\text{Energy}_{\text{product oil}}}{(\text{Energy}_{\text{bio-oil}} + \text{Heat}_{\text{inputs}})} \quad (1)$$

Where $\text{Energy}_{\text{product oil}} = m_{\text{product oil}} \text{HHV}_{\text{product oil}}$, $\text{Energy}_{\text{bio-oil}} = m_{\text{bio-oil}} \text{HHV}_{\text{bio-oil}}$

According to the calculation results, the product oil recovered 34% energy of the energy inputs. The recovery rate of CGF run was a little higher than the PGF run, but the gap is limited. Since the catalyst in the PGF run can be reused and the separation temperature was lower than the the CGF, oil upgrading at a lower separation temperature is a rational choice.

4. Conclusions

The bio-oil can be upgraded in a process with two heating unit with or without zeolite catalyst. The main reaction of the cracking is deoxygenation of phenols. The zeolite catalyst contributes to promote the deoxygenation rate. However, utilization of zeolite catalyst results in a decrease of the liquid product yield. As a liquid fuel, the properties of the catalytic cracked oil were better than the non-catalytic cracked oil. The hundreds of components in the raw bio-oil can be divided into 4

classes: small molecules, phenols, naphthalenes and macromolecules. Small molecules are not the main cause of the catalyst deactivation. Phenols slightly deactivate the catalyst. The contact of naphthalenes and macromolecules with zeolite is a big problem causing the deactivation. A lower separation temperature in the first heating unit helps to alleviate the inactivation reaction.

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Conflict of interest

All authors declare no conflicts of interest in this paper.

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