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Mercury in desulfurization gypsum and its dependence on coal properties in coal-fired power plants

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ABSTRACT

To disclose possible influencing factors on mercury (Hg) contents in flue gas desulfurization (FGD) gypsum of coal-fired power plants (CFPPs), 11 major CFPPs in Guizhou province of southwest China were surveyed for analyzing Hg contents in feed coal, limestone and gypsum as well as coal properties. It was found that Hg contents in the desulfurization gypsum of the 11 CFPPs varied greatly from 160 to 1482 μ g kg⁻¹, with an average of 595 \pm 353 μ g kg⁻¹. The majority of Hg in gypsum was introduced from the flue gas downstream of the particulate matter control devices, while a much lesser portion (average 3.43 \pm 3.85%) was stemmed from limestone. Hg content in gypsum has a strong positive correlation with chlorine content, a weak positive correlation with Hg content and a weak negative correlation with sulfur content in feed coal. Multiple regression analysis results showed that Hg and Cl contents in feed coal were the major determinants of Hg content in flue gas FGD gypsum despite the proportioning of Hg went in wet FGD system was not been evaluated. Results from the present study suggested that coal characteristics are important factors affecting Hg contents in gypsum.

1. Introduction

Mercury (Hg) is a highly toxic heavy metal due to its volatility, persistence and bioaccumulation [1]. Hg in air, most of which is in the form of gaseous elemental mercury (Hg⁰), has a lifetime of 0.5–2 years and thus can transport globally, making it a pollutant of global concern. The industrial sector of coal-fired power plants (CFPPs) is one of the main anthropogenic sources of atmospheric Hg emissions [2-6]. Hg emissions from flue gas of CFPPs are in the forms of Hg⁰, oxidized gaseous mercury (Hg^{2+}) , and particulate-bound mercury $(Hg_{(p)})$ [7]. Elemental mercury is exceedingly water-insoluble, whereas compounds of mercury, such as mercuric chloride, tend to be soluble or somewhat soluble [4-6,8-10]. Besides, compounds of mercury such as mercuric chloride, can readily adsorb on unburned carbon present within fly ash [4–6,8–10]. A cost-effective strategy to reduce Hg emissions from CFPPs is to transform Hg^0 into Hg^{2+} and $Hg_{(p)}\!,$ the forms that can be easily removed by existing air pollution control devices (APCDs), such as wet flue gas desulfurization (WFGD) systems and dust collectors [11,12].

WFGD system could co-remove highly soluble Hg²⁺, consequently producing mercury-laden byproducts [13]. The Hg removal efficiency

will be greatly increased once a system is equipped with selective catalytic reduction (SCR) devices, which enhance the oxidation of Hg^0 to Hg^{2+} [14]. FGD gypsum is an important byproduct of a WFGD system. Compared with natural gypsum, FGD gypsum has many advantages, such as abundance, uniform particle size, excellent chemical and physical properties, and high degree of purity, and is widely used in cement, concrete and wallboard production, structural fills/embankments, agricultural practice, soil stabilization, mining reclamation, and waste disposal in industrial landfills [15,16]. However, Hg in FGD gypsum may pose a high risk of Hg contamination during posttreatment of FGD gypsum [5,6,17–19], which could heavily hinder its commercialization due to tight quality standard for human health concern [20].

Hg concentration in FGD gypsum can vary substantially with different CFPPs, for example, from 10 to 1400 mg kg⁻¹ in different CFPPs in the U.S. [16], from non-detectable (ND) to 4330 mg kg⁻¹ (average 891 mg kg⁻¹) in 70 CFPPs in 20 provinces of China [21], and from 132 to 597 mg kg⁻¹ in seven CFPPs in Guizhou [22]. Moreover, the proportion of Hg retained in gypsum also varies greatly with different CFPPs, and the proportion could reach as high as 67% [22,23]. Numerous studies have investigated the synergistic effects of Hg

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Full Length Article





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removal across the APCD in CFPPs [24–26] and the desulfurization slurry condition effects on Hg content in gypsum [17], but few studies have examined the effect of coal properties, such as Hg, chlorine (Cl) and sulfur (S) contents in feed coal, on Hg content in gypsum. Because coal properties greatly affect the Hg removal efficiency of APCD [27], it likely also affects Hg content of gypsum, knowing that almost all Hg in power plant gypsum comes from coal. A previous study showed that Hg in limestone, which is the main desulfurizer in the WFGD system, was as high as 1296 μ g kg⁻¹ [28]. Therefore, sources of Hg in gypsum and possible influencing factors need to be investigated.

Guizhou is the largest coal-bearing province in South China [29], where coal is mainly formed in the Late Permian and featured with higher ash yields and sulfur contents than coals from other parts of China [30]. In 2017, 66 Mt coal was used in CFPPs, which is equivalent to 49.3% of the total coal consumption in this province [31]. Twenty CFPPs were operated in this province with an installation of 30.1 GW [31]. However, to date, there are only limited data regarding the local Hg content in FGD gypsum.

In this study, gypsum and the corresponding feed coal and limestone samples were collected from the 11 main power plants in Guizhou province. Hg contents in these solid samples were determined, the sources of Hg in gypsum were analyzed, and the effects of coal properties on Hg content were evaluated. The aim of this study is to explore the factors controlling Hg in desulfurization gypsum and lay a foundation for Hg control in the gypsum of CFPPs.

2. Methodology

2.1. Site description and sampling

Eleven main CFPPs in Guizhou province of southwest China were selected for investigation, and their locations are illustrated in Fig. 1. CFPPs 1# is located in the eastern part of the province, 2, 3 and 5# in the north, 4 and 6# in the central, and 7, 8, 9, 10 and 11# in the west. Information about the boiler type, capacity and APCDs is given in Table S1. Briefly, all CFPPs were equipped with a pulverized coal fired boiler, and the APCDs consisted of selective catalytic reduction (SCR), cold side electrostatic precipitator (C-ESP) or C-ESP combined fabric filter (FF) and WFGD. In each CFPP, only one unit was sampled since the feed coal, boiler type and APCDs are the same for different units. Solid samples, including the feed coal and limestone, were collected simultaneously with the gypsum, and each CFPP was sampled three times. To ensure the reliability of sampling, each sample was gathered by mixed with at least 9 subsamples collected within 2 days. In total, 33 gypsum, 33 feed coal, and 33 limestone samples were collected, placed in polyethylene ziplock bags, and stored in a cooler at 4°C for transportation. The sampling period lasted from August 2016 to May 2019.

Pulverized coal furnaces account for over 90% of the installed capacity of CFPPs in China [3], and the desulfurization method of CFPPs equipped with circulating fluid bed (CFB) boilers is mainly calcium desulfurization in the furnace without producing desulfurization gypsum. Moreover, only a part of CFPPs equipped with CFB is installed with WFGD, and existing results show that the content of desulfurization gypsum is very low (<20 ppb) [32]. Therefore, only the gypsum from CFPPs equipped with PC is discussed in this study.

2.2. Analysis methods

Solid materials including coal, limestone and gypsum were dried at 40 °C for 7 days before being ground into small pieces (<0.150 mm). Total Hg (THg) concentrations in soil samples were analyzed using a Direct Mercury Analyzer (Milestone DMA – 80, Italy) according to U.S. Environmental Protection Agency (EPA) method 7473. It's unique processing of the sample by thermal decomposition, amalgamation, and atomic absorption spectrometry allows for direct analysis of the sample matrices [33]. The proximate analysis method for feed coal samples was referenced from the Chinese national standard method GB/T 212-2008 [34]. Carbon (C), hydrogen (H) and nitrogen (N) contents in feed fuel samples were determined by an elemental analyzer (Vario MACRO Cube, Elementar, Germany), and the total sulfur (S) in feed fuel samples was measured based on the Eschka method GB/T 214 - 2007 [35]. The calorific value was determined by GB/T213-2008 [36]. The chlorine (Cl) concentration was determined with IC, and the detailed procedures are provided in Peng et al. [37].

2.3. Quality assurance and quality control

Quality control measures include method blanks, triplicates, matrix spikes and several certified reference materials. The glassware and vessels used for sample digestion were soaked in 20% nitric acid overnight and rinsed with deionized water. The reagents used are guaranteed reagent (GR). The limit of detection was 0.01 μ g kg⁻¹ for THg. During the digestion and analysis processes, system blanks, duplicate samples and certified reference materials (CRMs) were used to ensure quality assurance and quality control. CRMs for anthracite (GSB 06 – 2105–2007) and bituminous coal (GSB 06 – 2114–2007) were used during the proximate and ultimate analysis, and a recovery of 95–105% for different parameters was obtained. CRMs for coal (NIST 1632d), gypsum (NIST 2429) and limestone (JDo-1) were used for THg analysis, and the recovery of Hg in different CRMs was in the range of 92.2–117.4%. The relative standard deviation (RSD) of duplicate analysis for Hg concentration data in this study was<10%.



Fig. 1. Locations of the 11 CFPPs surveyed in Guizhou province.

3. Results and discussion

3.1. Hg contents in gypsum

The Hg contents in gypsum of the 11 CFPPs ranged from 160 in 5# to 1482 μ g kg $^{-1}$ in 8#, with an average of 595 \pm 353 μ g kg $^{-1}$ (Fig. 2 and Table S2), which was approximately 5.4 times and 8.5 times higher than the background soil of Guizhou province (110 μ g kg $^{-1}$) and of China (70 μ g kg $^{-1}$), respectively [38]. The Hg content in gypsum in six out of 11 CFPPs exceeded, while the average of the 11 CFPPs only slightly exceeded the risk screening value for soil contamination of agricultural paddy field land (0.5 mg kg $^{-1}$, pH \leq 6.5); but the average value is much lower than the risk intervention value for soil contamination of agricultural paddy field land (2 mg kg $^{-1}$) recommended by soil environmental quality: risk control standard for soil contamination of agricultural land (GB 15618–2018) [39]. The much higher Hg contents in CFPPs gypsum than background soils suggest potential Hg contamination in land use of FGD gypsum.

The large variations in Hg concentration in gypsum from different CFPPs have also been reported in previous studies (Table 1) [21,22]. Although Guizhou is located in the center of the Circum-Pacific mercuriferous belt from the perspective of global plate tectonics, and with the highest Hg content in coal (1.14 mg kg⁻¹) nationally [40], Hg contents in gypsum from CFPPs in Guizhou, as observed in the present study, were actually lower than some of the reported values in other parts of China [21,41-43], e.g., much lower than those in Shanxi (1453 \pm 48 µg kg⁻¹) [44] and Anhui (>2000 µg kg⁻¹) [21]. However, values from the present study were comparable with those reported in the U.S. $(10 \text{ to } 1440 \,\mu\text{g kg}^{-1})$ [16], and were much higher than those reported in some earlier studies in Guizhou (133 to 597 μ g kg⁻¹) [22,45,46] and China [47]. Comparing with the data of the same CFPPs a decade ago, the Hg contents in gypsum of CFPPs 6# (563 \pm 88 μ g kg⁻¹) and 1# (733 \pm 244 µg kg⁻¹) (Table S2) were both approximately two times higher now than previous reports [45,46]. This is likely due to the recent installation of the SCR system, which could promote the oxidation of Hg^0 to Hg^{2+} [27] and consequently lead to more Hg to be captured by WFGD system and stored in gypsum. Other studies listed in Table 1 [48–58], the number of CFPPs for sampling gypsum were all<4, and the Hg contents varied greatly between different gypsum samples. Note that previously reported Hg contents in gypsum, as listed in Table 1 were all lower than 6310 μ g kg⁻¹ [43].

3.2. Source analysis of Hg in FGD gypsum

It is generally believed that all Hg in gypsum comes from coal [59]. Hg in coal is released during combustion, enters into flue gas and bottom



Fig. 2. Hg content in FGD gypsum of 11 CFPPs.

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Literature reported Hg contents in FGD gypsum.

Area	Hg content $\mu g \ kg^{-1}$		Number of	Reference
	Range	Average	CFPPs	
Guizhou, China	176–1482	595 ± 353	11	This study
China	80–6310* 60–4190**	750* 510**	5	Wen M., et al. (2020) [43]
China	428.2*	-	1	Liu, S., et al. (2020)
Japan	1200	-	1	Sakusabe K., et al.
China	200–3850	-	3	Zhao, S., et al.
Guizhou, China	133–597	-	7	Liu, S., et al. (2018)
China	320	-	1	Li, J. and W. Jinman (2018)
Heibei, China	330–2400	-	11	Diao, X., et al.
China	750–3270	-	3	Zhu, ZW., et al.
China	190–3270	-	7	Zhu, Z., et al.
Shanxi, China	538–3976	1453 ± 48	12	Hao, Y. (2017) [44]
China	0 - 4330	891	70	Hao, Y., et al. (2016) [21]
American	10–1440	-	-	Watts, D. B. and W. A. Dick (2014) [16]
Zhejiang, Guizhou	610–1630	-	4	Sun, M., et al.
American	300	-	1	Wang, K., et al. (2013) [53]
China	50-800	-	9	Liu, X., et al. (2013)
China	640–700	-	2	Tang, Q., et al. (2012) [54]
American	355	-	1	Pasini, R. and H. W. Walker (2012) [55]
Spain	150-310	-	2	Rallo, M., et al. (2010) [56]
Guizhou, China CFPPs 6#	309–561	-	3	Wang, S., et al. (2010) [7]
Guizhou, China, CFPPs 1#	324–371	350 ± 20	1	Xu, W.(2010) [45]
Guizhou, China	231	-	1	Jiang, P., et al. (2007) [46]
American	202–205	-	2	Kairies, C. L., et al. (2006) [57]
American	126–162	-	2	Heebink, L. V. and D. J. Hassett (2005)

*Before and **After ultra-low emission technology (ULE) Retrofitting.

ash, and then distributes into different byproducts and exhausts. The main form of Hg removed by the WFGD system is Hg^{2+} , and the removal efficiency can be as high as 90% if considering Hg re-emission [60]. Previous studies [61,62] also showed that Hg^0 could also be removed in typical wet FGD system as Hg^0 present in the gaseous phase can be dissolved and oxidized to a high degree. All those results above indicated that Hg could be effectively removed by the wet FGD system from flue gas. Wet FGD is a very complex system, desulfurizing agents and additives may also bring Hg into this system. Limestone is an important desulfurizing agent, which could be transformed into gypsum (CaSO₄·2H₂O) when reacting with SO₂ following the reaction equation (1):

$$CaCO_3 + SO_2 + \frac{1}{2}O_2 + H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2\uparrow$$
(1)

Therefore, it is necessary to know the Hg content in limestone and its

contributions to Hg in the desulfurization product of gypsum. It can be seen from Fig. 3 that only a tiny fraction of Hg is found in limestone compared to that in gypsum. The Hg content in limestone ranged from 4 to 73 µg kg⁻¹ with an average of 22 ± 17 µg kg⁻¹, which is quite consistent with previous studies on the Hg content in sedimentary rock (22.6 µg kg⁻¹) in China [28]. To assess the contribution of Hg in limestone to Hg in FGD-gypsum, the ratio (\hat{I} ·) of Hg in limestone to Hg in the final FGD gypsum is calculated with the following equation (2):

$$\hat{\mathbf{l}} = \frac{c_l M_l}{c_g M_g} = 0.581 \frac{c_l}{c_g} \tag{2}$$

where c_l is Hg content in limestone (µg kg⁻¹), c_g is Hg in gypsum (µg kg⁻¹), and M_l and M_g are molar masses of limestone (100) and gypsum (172), respectively.

It can be seen from Fig. 3 and Table S3 that, although the average input ratio of limestone Hg to gypsum Hg is only approximately $3.03 \pm 3.40\%$, the highest ratio can reach 15.27%, suggesting that limestone could also be an important potential source of Hg in FGD gypsum.

3.3. Influencing factors on Hg content in gypsum

Many factors can affect Hg contents in gypsum, including APCDs, boiler types, additives, slurry conditions and coal properties, but all of which are through two aspects. One aspect is the total Hg and its speciation in flue gas that enters into the WFGD slurry, since WFGD could only effectively remove oxidized gaseous Hg (Hg²⁺). APCDs may greatly affect the Hg content, and species in desulfurization slurry, such as SCR, could promote the oxidation of Hg⁰ to Hg²⁺, and the average Hg⁰ oxidation rate could reach 71% with a range of 34–85% [63]. ESP or FF could capture over 99.9% of Hg^P and lead to approximately 29–67% reduction in flue-gas THg [63]. The other aspect is Hg distribution in wet flue gas slurry. Additives [17,64] and slurry conditions [65,66], including pH and ionic concentration, can directly affect the distribution of Hg in the desulfurized slurry by combining or reacting with Hg²⁺.

CFPPs are one of the main anthropogenic Hg emission sources worldwide [3]. Ultralow emission (ULE) technologies have been retrofitted in CFPPs in China since 2014 to reduce emissions of particulate matter, sulfur dioxide (SO₂) and nitrogen oxides (NO_x) [43]. Therefore, the APCDs of CFPPs are all well equipped with standardized operation and management (Table S1). In this study, as the 11 selected CFPPs have similar APCDs and all with relatively stable performance, the CFPPs were considered as black boxes when analyzing the effect of the main input parameters (coal properties) on the output parameters (gypsum



Fig. 3. (a) Hg content in limestone, and (b) the ratio (η) of Hg in limestone to Hg in the final FGD gypsum of 11 CFPPs.

Hg content) (Fig. S1). The coal properties parameters include Hg, Cl, S and Fe contents in coal. The proximate and ultimate analysis results of feed coal were shown in section S1 and Table S4 of supporting information. With exception of feed coal of CFPPs 10# and 11#, the feed fuels in most CFPPs are featured with high ash yields, low-medium calorific values, and somewhat high sulfur contents.

3.3.1. Coal Hg content

As almost all the Hg in FGD gypsum comes from feed coal, it is necessary to know the effect of coal Hg content on gypsum Hg content. A slight positive correlation ($r^2 = 0.168$, p < 0.05) was observed between coal Hg and gypsum Hg content (Fig. 4a), suggesting that Hg content in coal is not the sole major factor that affects the amount of Hg in gypsum.

3.3.2. Coal Cl content

A significant correlation ($r^2 = 0.45$, p < 0.05) was observed between Hg in gypsum and Cl content in coal (Fig. 4b), indicating that the amount of Cl in coal moderately determines the amount of Hg in gypsum. This result may be supported by several previous reports [49,67,68] that show HgClx was one of the dominant Hg species in gypsum. Cl in coal can be easily released into flue gas in the form of inorganic chlorides during coal combustion [69]. The presence of chlorine-containing species in flue gas will greatly promote the oxidation of Hg⁰ in post-combustion process [70], including the oxidation of Hg⁰ by SCR catalysts [71,72], and consequently greatly affect the forms of Hg in flue gas. It was commonly accepted that the forms of Hg in flue gas greatly affect the removal efficiency of Hg by APCDs [27,63], and it was also confirmed by a previous study that THg in WFGD slurry would increase when more oxidized Hg was present in flue gas [73]. Moreover, Cl in WFGD slurry could increase the Hg amount in gypsum as Cl could combine with Hg and finally enter gypsum [74,75]. Therefore, the existence of Cl in flue gas could affect not only the form and concentration of Hg but also Hg distribution in wet flue gas slurry. It is the result of a combination of factors.

3.3.3. Coal S content

It can be seen from Fig. 4c that there was a weak negative correlation between the S content in coal and Hg in gypsum ($r^2 = 0.145$, p < 0.05), suggesting that increasing the S content in coal could decrease Hg content in gypsum. A previous study [76] showed that acid gas SO₂ could promote the oxidation of Hg⁰ by fly ash, and consequently, more Hg was absorbed on fly ash and removed by dust-cleaning apparatuses such as ESP or ESP-FF, hence reducing the amount of Hg entering the WFGD system. Moreover, higher contents of S in coal may lead to higher SO₂ concentration in flue gas and consequently lead to lower pH value and higher S(IV) (SO_3^{2-} and HSO_3^{-}) concentration during the absorption process in WFGD slurry. It was confirmed by previous studies that relatively lower pH could promote Hg re-emission in wet flue gas slurry [77-79] and S(IV) (SO₃²⁻ and HSO₃⁻) was the main reducing substance of Hg^{2+} in WFGD slurry [66,80]. In summary, the existence of SO₂ in flue gas also affects not only the form and concentration of Hg but also Hg distribution in wet flue gas slurry. Moreover, the sulfur content of the coal determines the absolute amount of gypsum produced from the wet FGD system. The higher the gypsum mass flow, the lower its specific Hg content for constant Hg content of the fuel.

3.3.4. Coal Fe content

It can be clearly seen from Fig. 4d that there was no significant correlation between gypsum Hg concentrations and Fe content in feed coal ($r^2 = -0.029$, p > 0.05). Earlier studies have shown that Hg in coal is generally combined with pyrite [81,82] and oxidation of Hg⁰ increases with increasing amounts of magnetite in the ash of CFPPs [83]. It is easy to understand that, although increasing magnetite in fly ash will greatly promote Hg oxidation, the amount of magnetite in fly ash may hardly be affected by the coal Fe content. Instead, the burning condition likely plays a more important role than the coal Fe content on oxidation



Fig. 4. Correlation between gypsum Hg content and feed coal. (a) Hg content, (b) Cl content, (c) S content and (d) Fe content of 11 CFPPs.

of Hg^0 . It should also be noted that only iron oxide with a spinel-type structure is active in fly ash with respect to Hg^0 oxidation [83].

3.3.5. Multiple regression analysis

To further explore the influence of coal characteristics on Hg content in FGD gypsum, multiple regression analysis was conducted, which showed coal Hg content and Cl content as the major determinant factors of Hg content in FGD gypsum. A regression equation is thus developed as follows:

$$c_{g} = -188.65 + 2.40c_{Cl} + 1.12c_{CHg}(R^{2} = 0.541, p < 0.05)$$

Where c_g is Hg in gypsum (µg kg⁻¹), c_{Cl} is Cl in coal (mg/kg), and c_{CHg} is Hg in coal (µg kg⁻¹).

It also should note that mercury is present at trace levels in both coal and coal byproducts, present as multiple species and the measurement of this element in these complex solid and liquid matrices is difficult [5,6]. Besides, coal and coal byproducts are not homogeneous materials, and this factor further impacts the successful closure of a mercury mass balance around all or part of a CFPPs.

4. Conclusions

This study analyzed the Hg content in FGD gypsum from 11 CFPPs in Guizhou Province, explored the source of Hg in gypsum, and evaluated the influence of feed coal characteristics on the Hg content in gypsum. Results showed that the Hg content in gypsum ranged from 160 to 1482 μ g kg⁻¹ with an average of 595 \pm 353 μ g kg⁻¹, which was much lower than the reported data of some provinces in China. Hg concentration in FGD gypsum varied substantially with different CFPPs. The Hg content in FGD gypsum introduced by limestone can reach up to 15.27% with an average of 3.43 \pm 3.85%, suggesting limestone as a potential source of Hg in FGD gypsum. The feed coal characteristics may significantly affect the Hg content in gypsum, as demonstrated by a significant positive correlation with the coal chlorine content, a slightly positive correlation with the coal Hg content, and a slightly negative correlation with the coal S content. Hg and Cl contents in coal have been proved to be the major factors determining Hg contents in FGD gypsum by multiple regression analysis. Knowledge generated from the present study lays a

foundation for the regulation and evaluation of Hg content in CFPPs FGD gypsum. Considering the small amounts of data used in this study and possible uncertainties during the analysis process, future studies using isotope-tracer technology should be conducted to confirm the conclusions generated here. And the proportioning of Hg in wet FGD depends on numerous further parameters, not within the scope of this study which needs to be discussed in further work.

CRediT authorship contribution statement

Qingfeng Wang: Methodology, Investigation, Data curation, Formal analysis, Writing - original draft. **Dan Wang:** Investigation, Software, Visualization. **Zhonggen Li:** Conceptualization, Writing - review & editing. **Leiming Zhang:** Conceptualization, Writing - review & editing. **Xinbin Feng:** Conceptualization, Resources, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2021.120413.

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