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Pyrolysis of Empty Fruit Bunches to Bio-Oil Using Combination of ZSM-5 and Spent FCC Catalysts

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Abstract. The objectives of this work were to generate bio-oil with optimum yield and specifications, by studying the effect of catalysts of ZSM-5 and spent FCC, the effect of combination of ZSM-5 and spent FCC catalysts, and the characteristics of bio-oil produced. In this work, the effect of combination of the two catalysts was studied with variation of weight ratio of ZSM-5 to spent FCC catalyst at 10:90, 20:80, 30:70, 40:60 and 50:50. The temperature was set at 400 and 500 ºC. The weight ratio of empty fruit bunches to the catalyst was 10:1. The results show weight ratios of combination of ZSM-5 and spent FCC of 10:90 and 50:50 at temperature of 500 °C are the best two combination ratios giving high yield of bio-oil products of 48.88 % and 47.49 %. Bio-oil resulted from combination of ZSM-5 and spent FCC catalysts with weight ratio of 50:50 at 500 ºC and weight ratio of 20:80 at 400 ºC showed two highests selectivity of phenolic compounds with peak area of 59.85 % and 55.63 % respectively, with heating value of 26.94 MJ/kg and 24.28 MJ / kg, respectively and average density of the two results at 1.03 g/cm^3.

Keywords: Catalytic pyrolysis, ZSM-5, spent FCC, empty fruit bunches,bio-oil

INTRODUCTION

Biomass pyrolysis is a thermal decomposition reaction of organic matter at intermediate temperatures between 400–600 ºC under the atmosphere of a non-oxygen state that produces bio-oil, solid residue and uncondensable gas [1-2] and this process is considered to be one of the most suitable methods to produce bio-oil from biomass with high yield and quality [3].

The development of bio-oil production processes from biomass using solid catalyst of ZSM-5 modified with heavy metals has begun to be widely studied by researchers. Catalytic cracking can reduce reaction temperature required. According to Wang et al. and Zhang et al. the presence of catalyst increases the specific reaction rate and can improve the quality of of bio-oil product [4-5]. Catalyst of ZSM-5 modified with Ni metal produced lots of aromatic hydrocarbons [6]. Sample of ZSM-5 desylicafication with alkaline solution give best catalytic performance which increases in aromatic production and BTX selectivity [7]. Che et al. reported that metal oxide catalysts such as CaO, Al_2O_3 with or without combination with ZSM-5 can convert pyrolysis vapor into aromatic hydrocarbons [8]. Substances like CaO is very good as promoter for increasing aromatic production, whilst Al_2O_3 is better in removing oxygen in oxygenated components. Combination of CaO and ZSM-5 can increase the selectivity and product yield of aromatic hydrocarbons at 6.14 % higher than using only ZSM-5. On the contrary, according to Paasikallio et al. the method of combining CaO and ZSM-5 catalysts produced lower yields of aromatic

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hydrocarbons, because the alkaline earth metal deposited on ZSM-5 decreases the activity of the catalyst resulting in poisoning the acid sites [9]. Soongprasit et al. used the fly ash-ZSM-5 to produce ketone compounds up to 79.4 % of the raw material of biomass from *Millettia pinnata* waste [10].

The use of HZSM-5 and off-grades catalyst such as spent FCC which was by-product from oil refinery, has been investigated by Ro et al. [11]. The spent FCC catalyst has high potency for catalytic pyrolysis of polymeric materials, even though its catalytic activity is lower than the original FCC catalyst. This is because it still has high acidity, which can improve aromatization reactions of pyrolysis vapors. Catalyst of FCC consists of zeolite-Y crystals which are spread in the active matrix of silica-alumina-clay [12]. Zeolite-Y has large surface area and high pore volume which are mostly still empty and can be utilized [13]. From the work of Ro et al. [11], between the varied kinds of catalysts applied in this work, HZSM-5 and spent FCC presented a higher cracking performance compared to bentonite, dolomite, and olivine. The use of spent FCC catalyst in EFB pyrolysis displayed a higher selectivity toward phenol and alkyl phenol, whilst the use of HZSM-5 showed higher selectivity to aromatic hydrocarbons. Both catalysts of spent FCC and HZSM-5 can produce bio-oil from EFB with high calorific values. Spent FCC produces less aromatic hydrocarbons than HZSM-5, yet it has higher performance in the production of phenols and alkyl phenols [11]. Catalytic pyrolysis process can be improved by the use of very active and inexpensive catalysts which can produce bio oil in large quantity at lower cost. The use of combination of spent FCC and ZSM-5 as catalyst can be a promising answer to it, and this is the jewel of this study.

MATERIALS AND METHOD

Raw Material

Raw material pretreatment: empty fruit bunches obtained from PT. Perkebunan Nusantara VII Palembang was dried in an oven at temperature of 110 °C for 4 h, then was ground to particle size of 0.2–0.4 cm.

Catalyst

Catalyst of ZSM-5 (SiO_2 / Al_2O_3 = 20) was synthesized using Nazarudin method [14, 15] which was discussed in previous journal [16]. Pretreatment of spent FCC catalyst from PT. Pertamina RU III was activated using furnace at temperature of 550 ºC for 5 h. The weight ratio of combination of ZSM-5 catalyst and spent FCC catalyst were varied at: 10:90, 20:80, 30:70, 40:60, 50:50) (w/w).

Methods

The catalytic pyrolysis of EFB with catalyst of ZSM-5, spent FCC, and combination of ZSM-5 and spent FCC catalyst were carried out in a set of equipment as shown in Fig. 1.

The catalyst and empty fruit bunches with weight ratio of 1:10 (w/w) were fed into the pyrolysis reactor, which is a fluidized bed reactor, at atmospheric pressure. The furnace was heated at 400 °C and 500 °C. During 1 h reaction time, the pyrolysis vapor product going out from the reactor was condensed in a reflux condenser, and the uncondensable gas was catched to the gas storage. After completion of the experiment, the result of solid residues and condensed bio-oil were weighed. The uncondensable gas was determined by calculating the difference between the weights of solid residue and the liquid reactant. To get accurate results, the composition of bio-oil product was analyzed using GC-MS (Gas Chromatograph Mass Spectrometry). The calorific value of the bio-oil product was analyzed using Parr 6400 Bomb Calorimeter. Bio-oil density was measured using pycnometer.

RESULTS AND DISCUSSION

The Effect of Using ZSM-5 and Spent FCC Catalysts and the Combination of Them at Process Temperature of 400 °C

The pyrolysis process of empty fruit bunches (EFB) was carried out without catalyst, with ZSM-5 and spent FCC catalysts and the combination of ZSM-5 and FCC. The temperature of the reaction was initiated at 400 ºC. The results of the experiment are shown in Fig. 2 below.

It can be seen in Fig. 2, that pyrolysis at 400 ºC with no catalyst resulting in lower yields of bio-oil than process using catalyst, with higher yields of uncondensable gas than process using catalyst and not very much different yields of solid residue with the process using catalyst. The performance of the ZSM-5 catalyst was better than spent FCC. The products from ZSM-5 are 38.067 % of bio-oil, 32.40 % of solid residue and 29.53 % of uncondensable gas, whilst the products from spent FCC catalyst are 34.2 % of bio-oil, 27.2 % of solid residue and 38.2 % of uncondensable gas. Catalyst of ZSM-5 has microcrystalline structure and pores that can accommodate reactant molecules to react in the active site of the catalyst [17]. This causes ZSM-5 to be the most efficient catalyst, not only for biomass catalytic pyrolysis, but also for the production of aromatic hydrocarbons [18].

Combinations of ZSM-5 catalyst with spent FCC give higher yields bio-oil product than solid residue and uncondensable gases. The higher the ratio of spent FCC to ZSM-5, the higher the bio-oil produced and the lower the uncondensable gas produced.

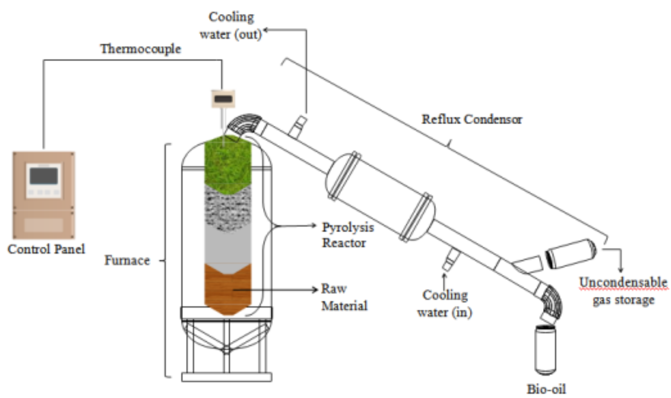

FIGURE 1. Schematic diagram of equipment used for catalytic pyrolysis of EFB.

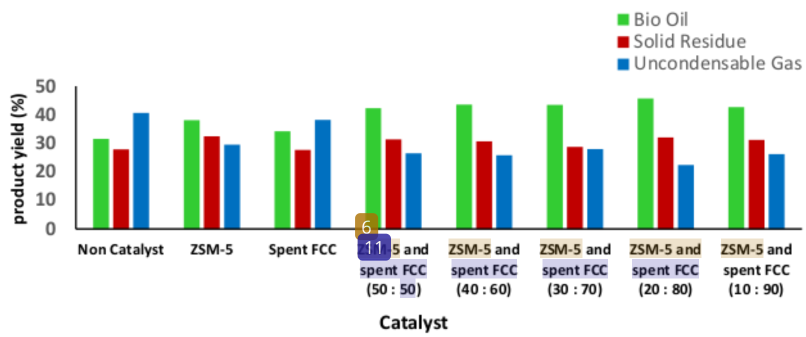

FIGURE 2. Product yield of non catalytic (thermal) pyrolysis and catalytic pyrolysis of EFB at 400 ºC.

The Effect of Using ZSM-5 and Spent FCC Catalysts and the Combination of Them at Process Temperature of 500 °C

The effect of increasing temperature and the presence of spent FCC catalyst in the pyrolysis of EFB were not much significant. Without catalyst, the yield of thermal pyrolysis of bio-oil is only 42.50 %. With ZSM-5 catalyst, the yield of bio-oil increases to 45.867 %, whilst with spent FCC catalyst the yield is the same as without catalyst, only 42.38 %. This means that the role of spent FCC is not significant because spent FCC is an off-grade catalyst and caused by coke content deposited on spent FCC catalyst. Even if spent FCC can give an increase in yield for bio-oil production when it is combined with ZSM-5 at weight ratio of 50:50, giving increase in bio-oil yield of around 6 % when compared to using only ZSM-5 catalyst. This fact can be seen in Fig. 3.

At combination of weight ratio of 50:50 of ZSM-5 and spent FCC, the yield of bio-oil products increases to 48.88 %, with solid residue of 28.67 % and uncondensable gas of 22.45 %. The greater the percentage of spent FCC, the higher the residual solid and uncondensable gas produced and the lower the bio-oil produced. This showed that ZSM-5 catalyst has an important role in the pyrolysis. Kim et al. [19] stated that at temperature of 500 ºC the decomposition of biomass has not happened significantly even it has used catalyst. The increase of bio-oil products yields from pyrolysis using combination of ZSM-5 and spent FCC catalyst at weight ratio of 50:50 was caused by spent FCC catalyst which still has high acidity which can improve the aromatization reaction of the pyrolysis vapor, which is condensed as bio-oil product. It is hoped that there will be specific combination of the two catalysts may produce the highest bio-oil product yield. The best 3 combinations of ZSM-5 and spent FCC catalysts were 20:80 at 400 ºC, and 50:50 and 10:90 at 500ºC. These are because the role of ZSM-5 is strongly influenced by the increase of temperature, with higher temperature resulting in the less ZSM-5 needed to produce high bio-oil yields.

Gas Chromatography–Mass Spectrometry (GC-MS) Analysis

From all the research data, three bio-oil samples from catalytic pyrolysis of EFB were analyzed using GC-MS to find out the composition of the bio oil produced. They are the samples from the pyrolysis using ZSM-5 at 500 ºC (Fig. 4), combination of ZSM-5 and spent FCC with weight ratio of 50:50 at 500 ºC (Fig. 5), and combination of ZSM-5 and spent FCC with weight ratio of 20:80 at 400 ºC (Fig. 6).

There are 75 readable peaks from GC-MS chromatogram of bio-oil product from catalytic pyrolysis using ZSM-5 at 500 ºC in Fig. 4. Among them were two peaks having area of > 10 %. The fifth peak with area of 14.89 % belongs to phenol. Meanwhile, the peak number 46 with area of 13.81 % belongs to phenolic compound of phenol, 2,6-dimethoxy. Other three highest peaks were peak number 16 with area of 9.69 % belongs to phenolic compuond of phenol, 2-methoxy, peak number 53 with area of 3.17 % belongs to 1,2,4-trimethoxybenzene, and peak number 8 with area of 3.23 % belongs to butyric acid hydrazide.

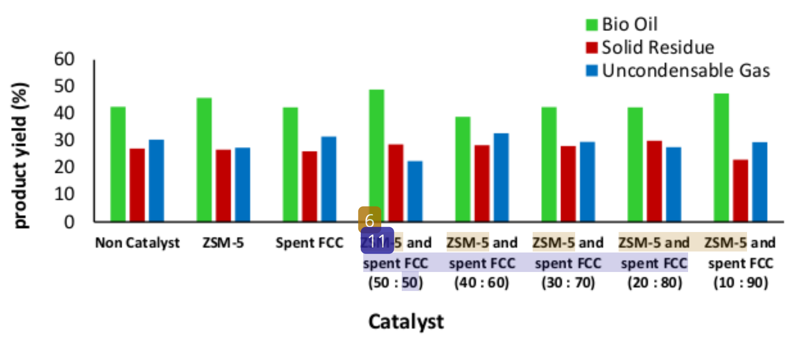

FIGURE 3. Product yield of (non catalytic) thermal and catalytic pyrolysis of EFB at 500ºC.

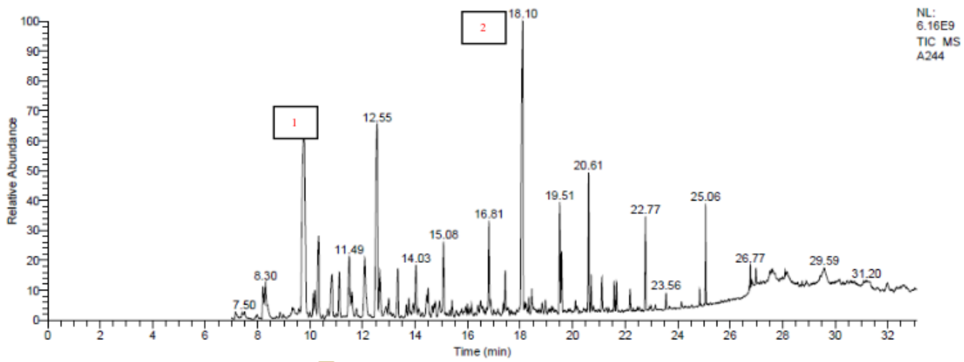

FIGURE 4. Chromatogram of bio-oil from catalytic pyrolysis of EFB using ZSM-5 catalyst at 500 ºC.

Figure 5 shows the results of the GC-MS chromatogram of bio-oil produced using combination of ZSM-5 and spent FCC catalysts with weight ratio of 50:50 at 500 °C. Among 75 readable peaks, there were two peaks with area of > 10 %. The fifth peak with area of 13.97 % belongs to phenol, the peak number 42 with area of 11.84 %, belongs to phenol, 2,6-dimethoxy. There are three other highest peaks which are peak number 15 with area of 7.12 % belongs to phenol, 2-methoxy, peak number 56 with area of 3.65 % belongs to 5-tert-butylpyrogallol, and peak number 50 with area of 2.81 % belongs to 1,2,4-trimethoxybenzene.

Figure 6 presents the results of GC-MS chromatogram of bio-oil produced using combination of ZSM-5 and spent FCC catalyst with weight ratio of 20:80 at 400 °C. Among 77 readable peaks, there were two peaks having area >10 %. Peak number 3 with area of 15.21 % belongs to phenol, peak number 44 with area of 11.6 % belongs to phenol, 2,6-dimethoxy. There are three other highest peaks of peak number 76 with area of 5.78 % belongs to 16-hentriacontanone, peak number 52 with area of 3.11 % belongs to benzene, 1,2,3-trimethoxy-5-methyl, and peak number 61 with area of 3.20 % belongs to hexadecanoic acid, methyl ester.

The high content of phenolic compounds in bio-oil samples (from Fig. 7) comes from lignin content in empty fruit bunches as raw material. Lignin with three phenylpropane units can be depolymerized to various phenolic compounds, such as benzenediol, methoxyphenol, alkylphenol [20].

Ro et al. [11] used HZSM-5 catalyst with weight ratio of catalyst and EFB raw material at 1:1. The bio-oil produced from EFB catalytic pyrolysis, showed high selectivity to aromatic hydrocarbons with peak area of 40.4 %. If uses spent FCC catalyst, the high selectivity comes from phenolic compounds with peak area of 57.5 %. In this present study, we used weight ratio of 1:10 for the catalysts and EFB raw material, resulting in bio-oil products with high selectivity to phenolic compounds. The high content of phenolic compounds in bio-oil samples comes from lignin content in empty fruit bunches as raw material. Huang and Yuan reported that the composition of bio-oil from sawdust dominantly was of phenols. When the raw material is from mixture of sawdust and rice straw, which lignin was the main component, underwent a process of dehydration, hydrolysis and dealkylation to produce phenols, alcohols, and acids; alcohols or added solvents of ethanol and acids can react further to produce esters [21].

There are two pathways for cellulose pyrolysis (Fig. 8) [22]. One involves dehydration and charring reactions of anhydrocellulose to form chars, tars, carbon oxides, and water, whilst the other involves depolymerization and volatilization of levoglucosan to form chars and combustible volatiles [23-24]. The first pathway would be expected to occur at lower temperatures when the dehydration reactions are dominantly and thus delays the initial process, correspond to reduce the degree of polymerization and the formation of the anhydrocellulose. The second pathway results in the formation of oligomeric species as well as their degradation products, which quickly converts into vapor [25].

Density and Calorific Value Analysis

The average value of bio-oil density from catalytic pyrolysis of EFB at two temperatures using three types of catalyst, namely ZSM-5 catalyst at 500 ºC, combination of ZSM-5 and spent FCC catalysts at weight ratio of 20:80 at 400 ºC, and combination of ZSM-5 and spent FCC catalysts at weight ratio of 50:50 at of 500 ºC is 1.03 g/cm^3.

This value indicates that bio-oil density still does not meet the specification of ASTM standards D4052, which requires bio-oil standard density at the range of 1.1–1.3 g/cm^3. This was caused by phenolic compounds contained in

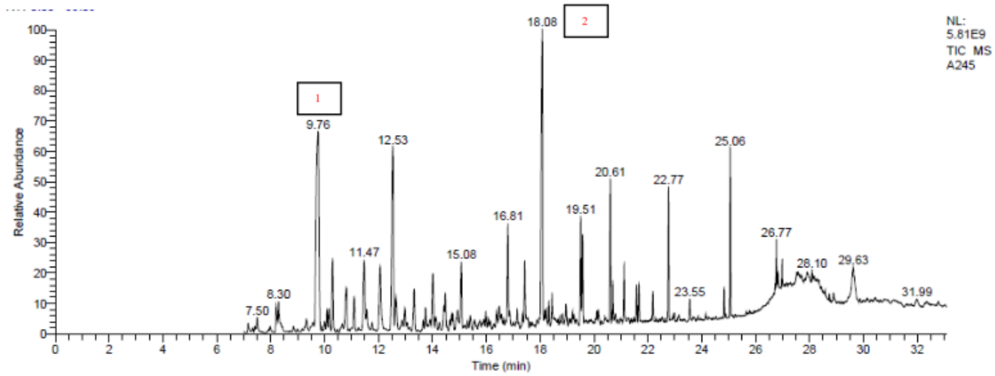

FIGURE 5. Chromatogram of bio-oil from catalytic pyrolysis of EFB using combination of ZSM-5 and spent FCC with weight ratio of 50:50 at 500 ºC.

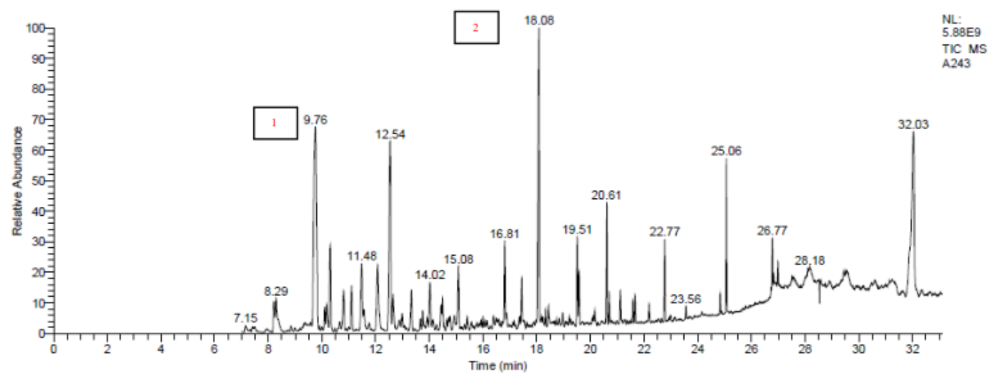

FIGURE 6. Chromatogram of bio-oil from catalytic pyrolysis of EFB using combination of ZSM-5 and spent FCC catalysts with weight ratio of 20:80 at 400 ºC.

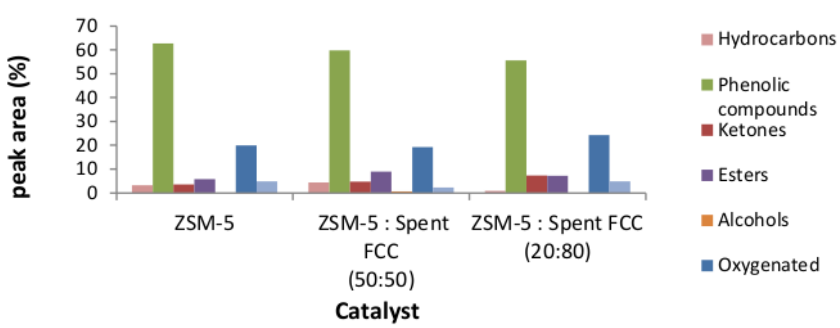

FIGURE 7. Percent of GC/MS peak area of chemical groups in organic phase of bio-oil from catalytic pyrolysis of EFB.

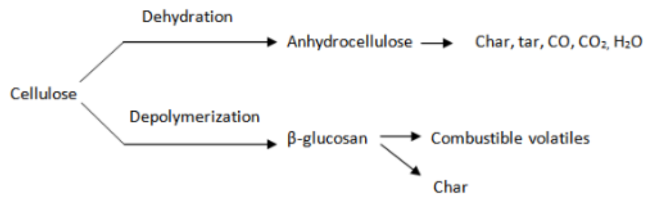

FIGURE 8. Pathways for cellulose pyrolysis.

the bio-oil. The density of phenol compounds is around 1.07 g/cm^3 and contributes to the specific gravity of bio-oil, resulting in bio-oil with density close to phenol. The heating values of the above three samples are 24.50 MJ/kg from samples using ZSM-5 catalyst at 500 °C, 24.28 MJ/kg from sample using combination of ZSM-5 catalyst and spent FCC with a ratio of 20:80 at 400 °C, and 26.94 MJ/kg from combination of ZSM-5 and spent FCC catalysts ith weight ratio of 50:50 at 500 °C. These values indicate that the heating values have met the specifications of bio-oil of ASTM standard D240, >15 MJ/kg. Ro et al. [11] in their work, have carried out experiments on the catalytic pyrolysis of EFB using HZSM-5 and spent FCC catalysts have produced bio-oil with heating value of 31.18 MJ/kg and 28.44 MJ/kg respetively.

CONCLUSION

The weight ratio combinations of ZSM-5 and spent FCC catalysts of 10:90 and 50:50 at 500 ℃ are the best two composition ratios producing high yields of bio-oil at 48.88 % and 47.49 %. The selectivity of phenolic compounds in bio oil from catalytic pyrolysis using combination of ZSM-5 and spent FCC catalysts with weight ratio of 50:50 at 500 ℃ and combination of ZSM-5 and spent FCC catalysts with weight ratio of 20:80 at 400 ℃ correspond to peak area of 59.85%, and 55.63 % respectively. These samples have average density of 1.03 g/cm^3, with heating value of 26.94 MJ/kg and 24.28 MJ/kg respectively.

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