

ETM0001 Catalytic Fast Pyrolysis of *Leucaena Leucocepphala* in Fluidised-bed Reactor with In-situ and Ex-situ Vapors Upgrading

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Abstract

This research aims to study the effects of pyrolysis temperature, effects of catalyst positions and effect of condensation on the product yield with a heating value and chemicals compound in bio-oil. The fast pyrolysis of *leucaena leucocepphala* were vapors upgrading to the bio-oil with in-situ and ex-situ in a fluidised-bed reactor. The fast pyrolysis process was used as silica sand for heat transfer medium in primary reactor. The glass wool was used hot filter medium in secondary reactor. While, the in-situ upgrading to catalyst in primary reactor. The ex-situ was upgraded to use a catalyst in secondary reactor. The results showed that maximum bio-oil yields of ~65 wt% at 500°C and get a higher heating value (HHV) of ~30 MJ/kg, when applied the ex-situ upgrading to obtaining the bio-oil yields decreased to 57 wt%. However, a HHV of the bio-oil were increasing to 38 MJ/kg and it has higher an aromatics hydrocarbons compound such as C_6H_{14} , C_7H_{14} , C_4H_{10} , C_5H_{12} , C_8H_{16} and $C_{20}H_{38}$.

Keywords: Ex-situ upgrading, Fast pyrolysis, In-situ upgrading, Leucaena leucocepphala, Natural zeolite.

1. Introduction

The fast pyrolysis of biomass is very quickly of biomass decomposing with a thermochemical at reaction temperatures of 400-600°C and fast of pyrolysis vapour condensing into the bio-oil. The biomass is using fast pyrolysis process and, a leucaena leucocepphala Orrachon et al [1] have had to use the fluidised-bed reactor of fast pyrolysis with temperature at 4 level about 400, 450, 500 and 500°C. The pyrolysis temperature at 500°C a maximum bio-oil yield of 65 wt%. The heavy phase of the bio-oil had a higher heating value of 20 MJ/kg. This is a heat to low, to be used fuel, but a heating value of the bio-oil can be improved to increase by catalytic fast pyrolysis. According to the research reported of Putun et al [2] used a natural zeolite for catalytic pyrolysis of cottonseed cake in fixed-bed reactor. It was found that increase the heating value of the bio-oil from 30.9 to 36.8 MJ/kg.

In 2016, Luo & Resende, reported in-situ (primary reactor) and ex-situ (secondary reactor) are upgrading of pyrolysis vapors from beetle-killed trees [3]. They are showed that the in-situ upgrading to highest aromatic yield 25% obtained to the carbonaceous residues yield 41% from higher selectivity to xylenes and aromatics with nine carbons. While the ex-situ upgrading, to a highest aromatic yield at 22%, it is a higher selectivity to benzene and toluene. However, the research of Luo & Resende [3] has not studied the effects of pyrolysis vapour condensation with a water-cooled condenser and electrostatic precipitator (ESP) condenser.

Therefore, this research focuses on the study effect of pyrolysis temperature on 3 level including 400, 500 and 600°C. The effect of water-cooled condenser and ESP condenser on bio-oil yield and heating value of bio-oil. When, the natural zeolite catalyst applies for vapors upgrading catalytic fast pyrolysis of *leucaena leucocepphala* in fluidised-bed reactor with in-situ (primary reactor), in-situ & ex-situ (primary & secondary reactor) and ex-situ (secondary reactor).

2. Materials and methods

2.1 Biomass feedstock

The biomass samples employed in this research was used *leucaena leucocepphala* from Kalasin Province, Thailand. The biomass drying by sun-dried, ground and sieved into 0.6-3 mm. Preceding to fast pyrolysis experiments, the biomass samples was drying by oven method or standard method with temperature at 105°C for 24 hours to reduce the moisture content to 8.5 wt%. When analysis of heating value following DIN 51900 with S.M.D. Torino Bomb Calorimeter showed that a higher heating value of 13.7 MJ/kg.

2.2 Fluidising medium and catalysts

Silica sand was used as a fluidising and heat transfer medium. Preceding to every experiment, the sand was burnt at 575°C for 24 hours and sieved to a particle size of 0.2-0.4 mm. For non-upgrading experiment, approximately 500 g of sand was applied in primary reactor. While the natural zeolite catalyst was burnt at 500°C for 4 hours and sieved to a particle size of 0.2-0.5 mm for primary reactor and particle size of 0.5-3 mm for secondary reactor. For catalytic fast pyrolysis experiment, approximately 500 g of catalyst was applied to primary and secondary reactor.

2.3 Fast pyrolysis apparatus

Fast pyrolysis of biomass was performed in a fluidised-bed reactor unit, designed and constructed at



the Bioenergy and Applied Energy Research Lab, Kalasin University, Thailand. Its schematic diagram illustrated in Fig. 1 Its main components are a biomass hopper, a fluidised-bed reactor (primary reactor), two cyclone separators, a hot filter (secondary reactor), a water-cooled condenser, a ESP condenser and an ice/salt condenser.



Fig. 1 Schematic diagram of the fast pyrolysis unit

The biomass hopper made from a glass tube, the capacity of the *leucaena leucocepphala* could hold about 0.02 m³ into 2 kg. The biomass particles could be fed to the primary reactor by nitrogen flow entrainment via a feeding tube with a cooling jacket to prevent premature pyrolysis. The primary reactor, cyclones and secondary reactor were made from 304 stainless steel tubing. The primary reactor was used internal diameter of 100 mm and the height of 800 mm.

The first and second cyclone were designed to remove fine char particles from pyrolysis vapour and collect them in the char pot. The secondary reactor was a fixed bed. For non-upgrading experiment, about 50 g of glass wool put in the filter and changed to every run. While catalytic fast pyrolysis experiment, about 500 g of catalyst put in the reactor.

The bio-oil collection set were including a watercooled condenser (bio-oil pot 1), an electrostatic precipitator (ESP) condenser (bio-oil pot 2), and ice/salt condenser (bio-oil pot 3). The water-cooled condenser was a double tube heat exchanger. The ESP operated at ~15 kV DC was used to aid the bio-oil collection. The ice/salt condenser was used a glass tube heat exchanger, had temperature operated at ~15°C.

2.4 Fast pyrolysis experiments

The pyrolysis temperatures measured and controlled at Temp1 (Fig. 1) were set at 400, 500 and 600°C to determine the optimum temperature for higher bio-oil yield production. The optimum temperature was used for three experiments include the in-situ, in-situ & ex-situ and ex-situ upgrading fast pyrolysis.

For non-upgrading experiments, the temperatures of the cyclone and the hot filter (Temp2) were controlled at \sim 420°C to prevent re-condensation, repolymerisation or secondary cracking of the pyrolysis vapour. While catalytic fast pyrolysis experiments, the

temperature of Temp2 was controlled at 500°C. The nitrogen flow of the top (FC1) and the side (FC2) of the hopper about 5 L/min, whereas the fluidising nitrogen flow (FC3) at 20 L/min. For every experiment, approximately 1 kg of biomass is fed to the reactor at a feed rate of 1 kg/h. The total experimental run duration for 1 hour. When the pyrolysis experiment finished, the reactor and heated parts are leftwing to cool to room temperature. Then, the reactor unit were dismantled and weighed for mass balance calculation.

2.5 Mass balance

The liquid bio-oil, char and non-condensable gases are the main products from fast pyrolysis. The yields of each product were calculated by weighing all parts of the fast pyrolysis systems that mainly comprised of biomass, silica sand, catalyst, fluidisedbed reactor, cyclone separators, hot filter and product collection unit, before and after every experiment. The total bio-oil yields were determined as a liquid weight from the product collection unit including water-cooled condenser (bio-oil pot 1), ESP condenser (bio-oil pot 2) and ice/salt condenser (bio-oil pot 3). The char yields were the combined solid masses collected from the reactor, cyclones, char pot and transfer line. The gas yields were calculated by difference.

2.6 Heating value of bio-oil and char analysis

The higher heating value (HHV) of bio-oil and char were determined by an S.M.D Torino bomb calorimeter according to the DIN 51900 method. Approximately 1 g of bio-oil and char sample in a cap was placed in a bomb or reaction chamber. The bomb was filled with an excess amount of oxygen. The bomb was installed in a bucket filled with 2,000 ml of water. The bio-oil and char sample was ignited by an electrically heated wire. The change of the water temperature was recorded by a computerised system. The bomb calorimeter calibrated with benzoic acid.

2.7 GC/MS of bio-oil analysis

Bio-oil was diluted in methanol-dichloromethane (1:1) to obtain 10 wt% concentration. The samples were filtered through a Filtrex nylon filter with 0.2 µm pore size prior to the injection. The gas chromatography/mass spectrometry (GC/MS) analysis of bio-oil was conducted using an SHIMADZU Gas Chromatograph Mass Spectrometer model GCMS-QP2010. The separation was made on a 30 m \times 0.25 mm id Restex Rtx-5MS column (Restex, USA) with 0.25 µm film thickness. Its phase composition was 5% diphenyl -95%dimethylpolysiloxane. The GC oven temperature were held at 60°C for 2 min and programmed to rise from 60°C to 270°C at 5°C/min. The oven maintained at the final temperature for 5 min. The injector temperature was 270°C with a split ratio of 100. Helium was the carrier gas with a linear velocity of 40 cm/s. The capillary column was directly connected to a metal quardrupole mass filter with pre-rod Mass Analyser and Electron multiplier detector. The mass spectrometer was operated with electron impact (EI) mode at ion source and interface temperatures of 250 and 230°C, respectively,



with ionisation energy of 70 eV. The mass range from m/z 20 to 650 was scanned with a scan event of 0.5 s. The data acquisition and processing was performed SHIMADZU LabSolutions GCMS solution software. This method was suggested by Duanguppama et al [4].

3. Results and discussion

3.1 Effect of pyrolysis temperature and catalysts on products yields

Effect of the pyrolysis temperature on the product yields in Fig. 2 showed that the total of bio-oil yields were maximum increase from 53.4 to 64.7 wt%, and the gas yields slight increase from 18.9 to 20.6 wt%. When the pyrolysis temperature is increasing from 400 to 500°C. While the char yields were significantly reduced from 27.7 to 14.7 wt%. This is a resulting of a thermal chemical decomposition of cellulose and hemicellulose in leucaena leucocepphala more complete. However, the total bio-oil yield obtained from this research were also slightly lower compared with the research of Orrachorn et al [1]. Orrachorn et al [1] reported fast pyrolysis of leucaena leucocepphala particle size 0.25-0.5 mm in a fluidised-bed reactor at the pyrolysis temperature of 500°C have maximum bio-oil yields of 65.5 wt%. This is the effecting of biomass particle size to bio-oil decreased. Pattiya & Suttibak [5] was reported that the fast pyrolysis of cassava rhizome in fluidised-bed are increasing the particle size of the biomass from 0.25-0.425 to 0.425-0.6 mm, and the bio-oil yields dropped from about 64 to 56 wt% [5]. However, while the pyrolysis temperature was 600°C the total of bio-oil yields were dropped to 54.3 wt% and char yields also decreased to 12 wt%. While the gas yields rising up to 33.7 wt% the result of secondary was cracked reaction of vapors pyrolysis at the high temperature, the gas yield increased markedly.

When considering of Fig.2 (b) the heavy bio-oil yield was mainly proportion of the total bio-oil yield by the pyrolysis temperature of 500°C with the total bio-oil yields up to 64.7 wt% as a result the sum of the heavy and light bio-oil yields was 47.1 and 17.6 wt%, respectively.

For the effect of the pyrolysis temperature on the proportions of heavy bio-oil in Fig. 2 (c) shows that the water-cooled condenser can be condensing the bio-oil yield was higher than the ESP condenser. The pyrolysis temperature of 500°C has heavy bio-oil yields a maximum 47.1 wt% because of the heavy bio-oil yields from water-cooled condenser were maximum of 29.4 wt% and from ESP condenser maximum 17.6 wt%. Which, difference was expected as a consequence of water in biomass and reaction water in process condensed combined with heavy bio-oil from watercooled condenser at high. Since the report of Yin et al [6] reported that the fast pyrolysis of sweet sorghum bagasse in the fluidized bed reactor by using the watercooled condenser and the ESP condenser of bio-oil yields were different from 28.5 wt% to 7.4 wt%, and water content in bio-oil also different from 56.29 wt% to 6.08 wt%, respectively [6].



Fig. 2 Effect of pyrolysis temperature on (a) main product yields (b) yields of total bio-oil, heavy bio-oil and light bio-oil (c) faction of heavy bio-oil

The main product yields in Fig. 3 (a) showed that the catalytic fast pyrolysis applied the total bio-oil yields decreased obvious by the in-situ upgrading for reduced to 45.2 wt%. While the ex-situ upgrading to the total bio-oil yields reduced to 57.1 wt%. However, to using the catalyst in both of positions as a result and the total bio-oil dropped as low as 37.7 wt%. This the resulted of heat transfer efficiency of the catalyst was lower than silica sand. It can be seen from an in-situ upgrading. When applies the catalysts, the resulted was increased clearly on the char yield its showed that the biomass decomposition incomplete. In addition, the catalyst also the gas yield was increased obvious, especially with an in-situ catalyst on the gas yields were increased high as 35.5 wt%. The results of this research consistent with the reports of Lappas et al [7] at fast pyrolysis of Lignocell HBS 150-500 in a circulating fluid bed reactor by using the FCC catalyst in position of in-situ upgrading were decrease the bio-oil yields from 72.1 to 40.6 wt%, including char and gas



yields increased from 8.9 to 21.7 wt% and 9.5 to 14.2 wt%, respectively.



Fig. 3 Effect of catalytic fast pyrolysis on the yields of (a) main products (b) heavy and light bio-oil (c) faction of the heavy bio-oil

It's also found that the total bio-oil yield reduced the result of proportion heavy and light bio-oil yield were decreased when the applied catalytic fast pyrolysis. The resulted of using a catalyst with in-situ and ex-situ in the heavy and light bio-oil yields were decreased significantly that showed in Fig. 3 (b). The heavy bio-oil from water-cooled condenser belong to the total heavy bio-oil, it that mean when reducing of the heavy bio-oil from water-cooled condenser as a result, the total heavy bio-oil yield dropped. However, to applied the in-situ & ex-situ upgrading of heavy bio-oil yields decreases by, the heavy bio-oil yield from water-cooled condenser to 14.2 wt% and ESP condenser to 8.5 wt%.

3.2 Effect of pyrolysis temperature and catalysts on bio-oil properties

The Fig.4 shows that, the pyrolysis temperature increasing from 400 to 500°C. The HHV of the heavy bio-oil from ESP condenser were increased from 27.2 to 29.6 MJ/kg and a HHV of the heavy bio-oil from water-cooled condenser 18 to 22 MJ/kg. The HHV of the char was decreased from 20.5 to 17.2 MJ/kg. This was the resulted of organic compounds in biomass were decrease the thermos chemical decomposition more complete, more clearly.



Fig. 4 Effect of pyrolysis temperature on HHV of the heavy bio-oil

When the pyrolysis temperature increases at 600°C the HHV of the heavy bio-oil and the char were downward trend. The HHV of the heavy bio-oil were decreased because the reaction water of liquid bio-oil condensed. Garcia-Perez et al [8] have reported the temperature in the fluidised-bed reactor were increased from 500 to 580°C with a water content in bio-oil of mallee woody increased from approximately 12 to 17 wt%. The HHV of the heavy bio-oil decrease from 17.5 to 16 MJ/kg. However, the heavy bio-oil from ESP condenser on a HHV was higher than the heavy bio-oil from the water-cooled condenser that higher than the bio-oil derived from research of Orrachorn et al [1], the fast pyrolysis of *leucaena leucocepphala* in the same type reactor, which the HHV maximum to 20.3 MJ/kg.

In the Fig. 5 illustrate a HHV of char, the in-situ was higher heating value than ex-situ, because the char followed on the surface of catalyst affected of



efficiency heat transfer decreased, therefor the volume of char was increase. Lappas et al [7] used the FCC catalyst of the in-situ to fast pyrolysis of biomass in a circulating fluid bed reactor have had a char coke on catalyst about 4wt%.



Fig. 5 Effect of catalytic fast pyrolysis on HHV of the heavy bio-oil

The Fig. 5 shows that, the resulted of application catalytic fast pyrolysis in a HHV, the bio-oil derived from the condensation all of them were increased significantly. The HHV of bio-oil from ex-situ was higher than in-situ upgrading slightly, because there was difference on hydrocarbons elements. This information of major chemicals in heavy bio-oils in Table. 1 and the chromatograms of bio-oils in Fig. 6 indicates that the heavy bio-oils from water-cooled condenser of the in-situ upgrading were detected hydrocarbons, such as 2-methylhexane (C7H16), hexane (C₆H₁₄), 3-(1,5-dimethyl-hexyl) (C₃₀H₅₀), hexatriacontane $(C_{36}H_{74})$, methanopicene $(C_{30}H_{50})$, cyclopentane $(C_{22}H_{40})$ and cyclodocosane $(C_{24}H_{48})$. While the exsitu upgrading detected hydrocarbon group, as cyclohexene $(C_6 H_{10})$, heptadecane $(C_{17}H_{36}),$ cyclotetradecan (C14H28), tetracosane (C27H56), 2ethyl-3-methyl-1-butene (C_7H_{14}) , cyclohexadecane $(C_{16}H_{32})$ and octadecane $(C_{18}H_{38})$.

A major chemicals in heavy bio-oils from ESP condenser according to data in Table. 2, the chromatograms of bio-oils showed in Fig. 7 indicates that ex-situ upgrading detected hydrocarbons in the hexane (C_6H_{14}), 2-ethyl-3-methyl-1-butene (C_7H_{14}), 2-methylpropane (C_4H_{10}), pentane (C_5H_{12}), 3-octene (C_8H_{16}) and 9-eicosyne ($C_{20}H_{38}$) amount of them higher than in-situ upgrading. The ex-situ upgrading bio-oil of HHV were higher than in-situ upgrading slightly because concentrations of the hydrocarbons concentration. However, to combine with the in-situ & ex-situ upgraded the heavy bio-oils from water-cooled and ESP condenser both of them were higher energy.

Table. 1 Major chemicals in heavy bio-oils from water-cooled condenser identified by GC/MS

	Compound name	Formula	Chromatographic peak area (%)			
Retention time (min)			Non-upgrading	In-situ upgrading	In-situ & Ex-situ upgrading	Ex-situ upgrading
2.0	2-Methylhexane	C ₇ H ₁₆	1.6	4.9	3.2	3.8
2.2	Acetic acid	$C_2H_4O_2$	10.3	5.8	2.1	5.5
2.7	Hexane	C ₆ H ₁₄	2.7	10.0	9.5	4.9
3.0	Butanoic acid	$C_4H_8O_2$	2.1	1.2	0.4	0.7
7.3	Phenol	C ₆ H ₆ O	3.0	1.4	1.3	1.0
8.2	1,2-Cyclopentanedione	C ₆ H ₈ O ₂	3.2	1.5	1.8	1.8
31.1	n-Hexadecanoic acid	$C_{16}H_{32}O_2$	20.5	12.9	10.0	11.6
34.4	Oleic Acid	C ₁₈ H ₃₄ O ₂	34.4	17.3	12.7	17.5
34.8	Octadecanoic acid	C18H36O2	4.0	2.5	1.5	2.1
37.0	Octadecanedioic acid	C18H34O4	3.9	1.8	1.1	1.3
37.2	Eicosanoic acid	$C_{24}H_{48}O_2$	3.3	1.0	0.9	1.0
39.9	13-Octadecenal	C18H34O	2.5	1.7	1.1	2.2
40.1	Cyclohexanecarboxylic acid	$C_{13}H_{24}O_2$	1.5	1.2	0.4	1.2
41.8	3-(1,5-Dimethyl-hexyl)	C ₃₀ H ₅₀	0.0	8.3	2.3	0.0
42.9	Hexatriacontane	C36H74	0.0	5.8	5.6	0.0
43.8	Cyclohexene	C ₆ H ₁₀	0.0	0.0	5.9	2.9
44.1	Heptadecane	C17H36	0.0	0.0	6.6	7.0
44.2	Cyclotetradecan	C14H28	0.0	0.0	6.9	7.4
44.3	Tetracosane	C27H56	0.0	0.8	6.3	8.2
44.4	2-Ethyl-3-methyl-1-butene	C7H14	0.0	3.3	2.5	8.6
44.6	Cyclohexadecane	C16H32	0.0	0.6	2.9	7.8
44.7	Octadecane	C18H38	0.0	0.0	1.9	3.6
45.9	Methanopicene	C30H50	0.0	8.5	6.2	0.0
46.1	Cyclopentane	C222H40	0.0	4.4	3.2	0.0
46.8	Cyclodocosane	$C_{24}H_{48}$	0.0	5.1	3.7	0.0
47.5	Hexadecanoic acid	C35H68O4	3.6	0.0	0.0	0.0
47.7	Linoleic acid	C18H32O2	2.0	0.0	0.0	0.0
47.8	Hexadecanedioic acid	$C_{19}H_{36}O_4$	1.5	0.0	0.0	0.0
Total area (%)			100	100	100	100

Table. 2 Major chemicals in heavy bio-oils from ESP condenser identified by GC/MS

			Chromatographic peak area (%)			
Retention time (min)	Compound name	Formula	Non-upgrading	In-situ upgrading	In-situ & Ex-situ upgrading	Ex-situ upgrading
2.0	2-Methylhexane	C7H16	0.3	14.6	14.6	14.0
2.7	Hexane	C ₆ H ₁₄	0.0	7.6	8.4	8.7
3.7	2-Ethyl-3-methyl-1-butene	C ₇ H ₁₄	0.0	5.9	8.7	7.3
4.2	2-Methylpropane	C ₄ H ₁₀	0.0	6.1	4.7	7.1
5.1	1-Methylethenylcyclopropane	C ₆ H ₁₀	0.0	3.5	3.9	3.3
5.3	Pentane	C5H12	0.0	3.9	3.5	5.5
8.2	3-Octene	C ₈ H ₁₆	0.0	1.4	2.4	4.5
31.1	n-Hexadecanoic acid	C16H32O2	12.7	4.0	4.2	5.0
34.4	Oleic Acid	C18H34O2	13.6	4.4	2.0	2.5
34.8	Octadecanoic acid	C18H36O2	5.9	4.2	4.3	3.0
36.9	Octadecanedioic acid	C18H34O4	4.4	1.5	1.4	2.2
37.2	Eicosanoic acid	$C_{24}H_{48}O_2$	3.8	1.4	1.4	2.0
37.6	beta-sitosterol	C29H50O	4.1	0.0	0.0	0.0
39.9	9-Eicosyne	C20H38	0.3	6.2	4.8	7.0
40.1	Cyclohexanecarboxylic acid	C17H32O2	7.4	4.7	3.1	4.2
44.3	Campesterol	C28H48O	8.7	0.2	0.6	0.0
47.8	Tetratriacontane	C34H70	0.1	14.9	15.4	11.1
48.0	Hexatriacontane	C36H74	0.0	15.4	16.5	12.5
48.4	14-methyl-	$C_{28}H_{46}O_2$	24.6	0.0	0.0	0.0
48.5	Stigmast-5-en-3-ol, oleate	$C_{47}H_{82}O_2$	14.1	0.0	0.0	0.0
Total area (%)		100	100	100	100	





Fig. 6 Chromatograms of bio-oils produced from the water condenser when applied catalytic fast pyrolysis at a pyrolysis temperature 500°C





Fig. 7 Chromatograms of bio-oils produced from the ESP condenser when applied catalytic fast pyrolysis at a pyrolysis temperature 500°C

4. Conclusions

The optimum of the pyrolysis temperature for fast pyrolysis of *leucaena leucocepphala* in a fluidised-bed reactor 500°C, have a maximum of the total bio-oil yields 64.7 wt% and maximum the HHV of bio-oil from water-cooled 22 MJ/kg and ESP condenser 29.6 MJ/kg. Resulted of GC/MS analysis found that the bio-oil was higher acid. When applied the in-situ and ex-situ upgrading had total bio-oil yields were decrease to 45.2 and 57.1 wt%, respectively. However, the heavy bio-oil of the in-situ and ex-situ from water-cooled condenser has a HHV increased to 25.7 and 26.5 MJ/kg, while the heavy bio-oil of the in-situ and ex-situ from ESP condenser has a HHV increased to 37.0 and 38.1 MJ/kg. Which the GC/MS analysis found that the bio-oil acid decreased. The bio-oil of ex-situ upgrading had

hydrocarbons composition such as C_6H_{14} , C_7H_{14} , C_4H_{10} , C_5H_{12} , C_8H_{16} and $C_{20}H_{38}$ slightly higher as compared to bio-oil from the in-situ upgrading.

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6. References

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