CURRENT USES AND FUTURE CHALLENGES FOR ZEOLITE IN THE INDONESIAN OIL AND GAS PROCESSING INDUSTRY

by

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ABSTRACT

Oil and gas industry uses zeolite as an adsorbent to reduce moisture content of natural gas in LNG Plant, and as catalyst to convert the heavy petroleum fractions feeds into light clean fuels in refinery.

Low quality crude oil, low residual fuel demand, and an increased demands and specifications for light products (gasoline, kerosene, and diesel oil) and petrochemical products, future challenges for utilization zeolite as cracking catalyst in refinery are encouraging.

I. INTRODUCTION

Oil and gas industry processes naturally occuring hydrocarbons into fuels and petrochemicals. In general zeolite is used as adsorbent to reduce moisture content of natural gas in LNG plants, and in refineries this zeolite is used as catalyst for conversion of petroleum fractions into liquid fuels and petrochemicals [5,10].

Nowadays, refiners are facing a continuing need to add bottoms processing capacity as a result of gradually deteriorating crude oil quality and flat-to-declining demand for residual fuel oil [1]. Bottoms conversion into light valuable products can be done in three ways: i.e. carbon rejection, hydrogen addition, and gasification. Catalytic cracking and hydrocracking are catalytic processes for carbon rejection and hydrogen addition, respectively. These catalytic processes use acid cracking catalysts such as alumina-silicate of amorph or zeolite types [1,10,12].

Utilization of zeolite as cracking catalyst in Indonesian refineries, catalyst deactivation, improvement of natural mordenite for cracking catalyst and future challenges for utilization of zeolite in refineries are described briefly in this paper.

II. OIL AND GAS PROCESSING INDUSTRY IN INDONESIA

Out of 1,051.3 MBPSD total crude oil currently processed in Indonesian refineries, around 56.45 vol. percent is passed through catalytic processes to produce various fuel components. These comprise catalytic cracking (17,43 vol. %), hydrocracking (18,54 vol. %), reforming (13,78 vol. %), alkylation (0.18 vol. %), polymerization (2.53 vol. %), hydrotreating (42.93 vol. %) and merox (4.61 vol. %). Data on Indonesian and ASEAN refineries are presented in Table 1[9].

A. *Zeolite Catalyst*

Heavier feedstock and poorer feed quality can be converted into light products (gasoline, kerosene, diesel oil) by thermal and catalytic conversion. There are two types of catalytic conversion: i.e. catalytic cracking and hydrocracking processes.

1. Catalytic cracking processes

Catalytic cracking processes of heavy feedstock (heavy distillate, residue) using an acid cracking catalyst is extremely efficient in producing high octane gasoline and middle distillate with significant high olefin yield for motor fuel alkylation or oxygenates productions [5].

There are two units of catalytic cracking process (fluid cracking, riser cracking) with over 103,5 MBPSD total capacity in Indonesia (ASEAN 280.0 MBPSD) consisting of (processing vacuum distillate 15.8 vol % and atmospheric residue 84.2 vol%) using zeolite catalyst. Make up fresh catalyst is about 20.0 tonnes per day of fresh catalyst[8].

2. Hydrocracking process

Hydrocracking of heavy petroleum fractions to produce lighter distillate is a combination of catalytic cracking and hydrogenation and is carried out under substantial pressure using dual-function catalyst.

The balance between hydrogenation function and acid function in these catalysts may be substantially varied, such that a variety of feedstock can be processed, to produce a considerable variety of products. The acidic cracking function is usually similar to catalyst in catalytic cracking. The major hydrogenation function are Ni-Mo or Ni-W supported on this acid cracking catalyts [5].

Over 110,0 MBPSD total capacity heavy distillate is processed in four units of hydrocracking processes using Ni-Mo supported on zeolite or amorph to produce high quality middle distillate [9].

B. *Deactivation of Acidic Cracking Catalyst*

Sulfur, basic nitrogen compounds, sodium, nickel, vanadium, iron and copper in the heavy feeds of cracking process act as poisons to cracking catalyst. Asphalthene content of various crudes bottom is shown in Figure 1.

Sulfur, for instance, has little effect on the present alumina silicate catalysts, although it may affect the older natural clay catalysts, pre-

Table 1
Indonesian and ASEAN refineries

	INDONESIA		ASEAN	
	Unit	Capacity MBPSD	Unit	Capacity MBPSD
Unit	7	-	26	-
Crude Distillation	16	1051.3	46	3,874.4
Vacuum Cracking	6	274.1	22	952.58
Thermal Cracking	-	-	1	24.09
Visbreaking	1	45.0	7	279.3
Delayed Coking	1	35.0	1	35.0
Catalytic Cracking	2		10	
≅ Total		103.5		280.0
≅ Composition vol %				
- Heavy Distillate		15.8		43.89
- Atm. Residue		84.2		56.11
≅ Make up Fresh				
- Catalyst, ton/day		± 20.0		± 40.0
Hydrocracking	4	110.0	13	247
Reforming	7	81.801	35	449.531
Isomerisation	-	-	3	24.25
Alkylation	1	1.0	3	8.5
Polymerization	2	15.0	3	19.1
Hydrotreating	13	254.73	60	1,348.07
Merox	2	27.38	12	211.38

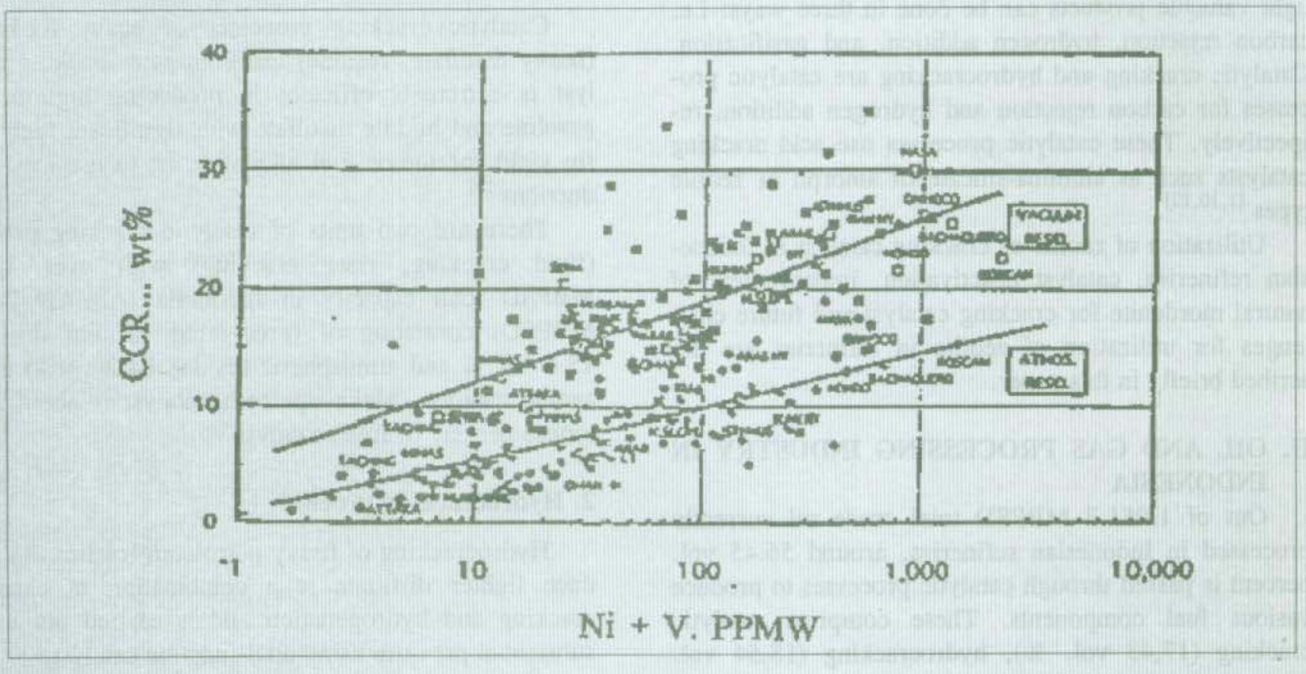

Figure 1
Influence of conradson carbon content of resid-feed cracking on the metal content

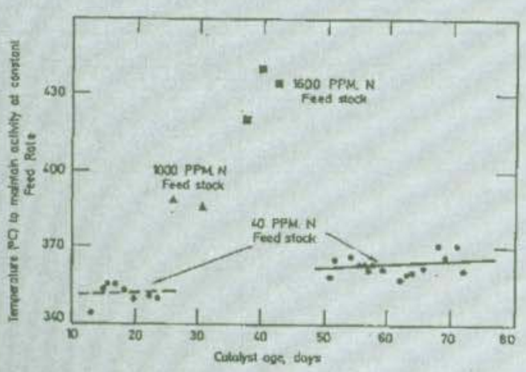

Figure 2
Effect of nitrogen on catalyst activity

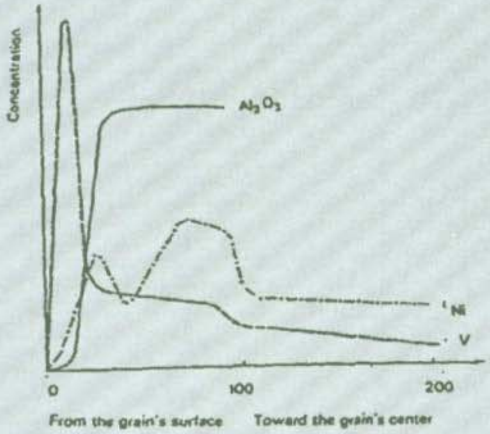

Figure 3
Distribution o Ni and V on the catalyst pores

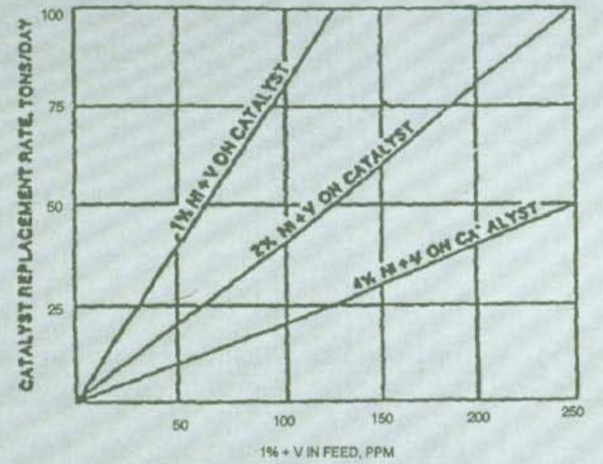

Figure 4
Influence of metal content of resid-feed cracking on the catalyst replacement of rate at given metal level of equilibrium catalyst

Table 2

Performance of treated natural mordernite

No.	Chemicals		Surface Area m^2/g	Acidity, mmol NH_3/g	Si/Al Ratio	N-Hexane Conversion mol %
1	NaOH	Non-treated	35.02	4.231	-	-
		Treated	98.2	6.642	-	-
2	HCl	Non-treated	180.01	2.6588	-	-
		Treated	251.7	4.4062	-	-
3	NH_4NO_3	Non-treated	180.01	2.6568	-	-
		Treated	220.3	4.4518	-	-
4	HF	Non-treated	73.8	-	-	-
		Treated	303.5	-	-	-
5	HCl	Non-treated	30	-	8	24
		Treated	130	-	15.42	50.52

Table 3

Hydrocracking of minas vacuum distillate with various catalyst acidity

Type of Products		Operating Temperature °C					
		390°		400°		410°	
		High Acidity	Low Acidity	High Acidity	Low Acidity	High Acidity	Low Acidity
Feedstock Conversion	wt%	40.43	40.53	54.38	50.93	83.19	63.01
Fractionated Liquid products							
IBP - 80°C (Light Naphtha) Yield	wt%	1.70	-	5.78	0.63	6.50	0.51
80° - 150° (Heavy Naphtha)							
Yield	wt%	43.53	2.30	8.45	4.53	15.73	7.66
Paraffin Content	vol%	48.27	34.84	54.75	48.27	55.24	54.75
Naphtha Content	vol%	40.50	51.72	24.45	40.50	26.14	34.45
Aromatic Content	vol%	11.23	13.34	11.80	11.23	8.62	11.80
150° - 250° (Kerosene)							
Yield	wt%	13.23	7.40	15.46	13.51	24.33	20.33
Smoke Point	mm	22.5	18.0	24.0	19.0	28.1	20.0
250° - 380° (Gas-Oil)							
Yield	wt%	20.11	30.81	21.59	31.90	23.54	34.34
Diesel Index		73.0	68.7	79.2	74.8	83.2	78.2

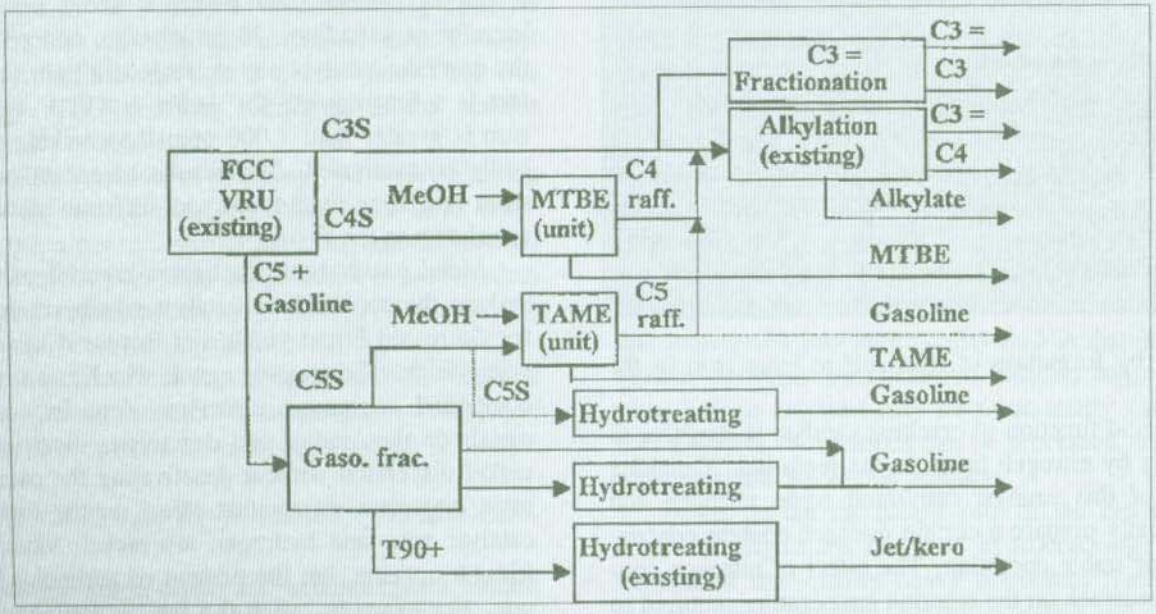

Figure 5
Cat. cracked gasoline fractionation for production of reformulated gasoline

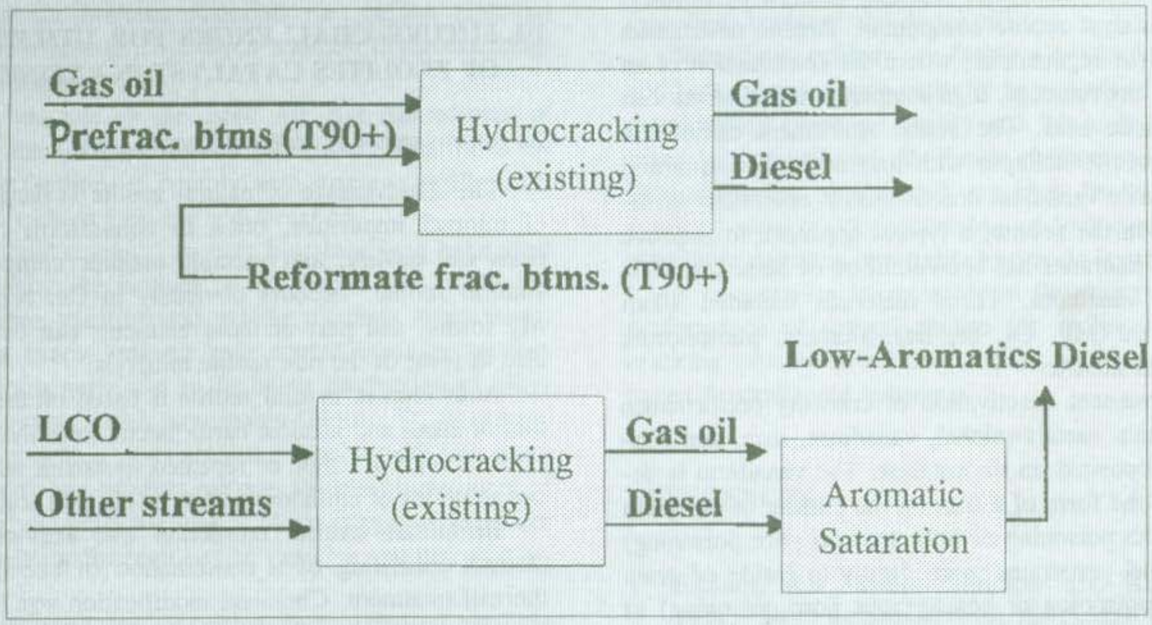

Figure 6
Hydrocracking process for production of reformulated diesel oil

Table 4
Operating conditions of continuous catatest unit

Operating Conditions		
Reaction		
Volume	cc	220
Inside Diameter	mm	19
Catalyst Volume	cc	5 - 40
Temperature	°C max	550
Pressure	bar	125

sumably by formation of iron sulfate from iron in the structure [4].

The acid function of cracking catalyst is sensitive to poisoning by nitrogen bases in the feedstock. Cracking activity of this catalyst can stand some nitrogen and may actually prepare a certain nitrogen content concentration for stable operation. The effect of nitrogen content of feedstock on the reaction temperature required to maintain a constant cracking activity is higher for amorph type than that for zeolite type (Figure 2).

Sodium deposition of the order of 1 wt. % on catalyst gives no appreciable effects. Sodium on the cracking catalyst is known to decrease the stability of the catalyst texture in thermal of hydrothermal treatments.

Vanadium deactivates cracking catalyst by destroying the catalyst zeolite component. Zeolite destruction begins in the regenerator, where the combination of an oxidising environment, high temperature and steam can form vanadic acid. The acidic attachment causes the zeolite pores to collapse with loss of surface area and acidity. Since vanadium deactivation is essentially an attachment on the zeolite, a typical approach to improve vanadium tolerance has been addition of basic materials to titrate vanadium. These materials included alkali earth metals (Mg, Ca, Sr, Ba), alumina, phosphorus, and barium titanate [11].

A permanent deactivation of cracking performance occurs when metals (nickel, vanadium, iron, and copper) are deposited on the catalyst. The vanadium is deposited in the form of a film on the outside of the grain (pore mouth poisoning or heterogenous pore poisoning) while nickel penetrates more deeply to inside of grain (uniform poisoning or homogenous pore poisoning) as illustrated in the Figure 3. Heterogenous pore poisoning gives lower pore effectiveness than does the homogenous pore poisoning [4,10].

Accumulation of these metals on the catalyst gives rise to the development of dehydrogenation activity of catalytic cracking catalyst leading to increased formation of gases and coke at the expense of gasoline yield. It can be inferred that nickel is about four times as harmful as vanadium. If the metallic concentrations in the cracking catalyst are expressed in ppm then the effect is a function of: $Cu + Fe + 4V + 14Ni$. If the sum is greater than 1,000 ppm the cracking catalyst is badly contaminated. The results of a catalyst replacement rate using resid feeds with different metal contents are shown in the Figure 4 [4,8].

Metal passivation deactivates harmful metal deposited on the cat-cracking catalyst which are responsible for decreased liquid yields and increased hydrogen and coke yields. The treating agent; which is an oil soluble compound containing antimony, deposits contaminant metals on the catalyst and deactivates them into poorer nickel dispersion without deactivating the catalyst. The most important metals that effect on the formation of catalyst coke and hydrogen are nickel, vanadium and iron. It appears that the present of antimony is important. For example, when 0,5 wt. % antimony was deposited, gasoline yield increased by 14%, coke yield decreased by 22% and hydrogen yield decreased by 57%. For this reason, catalysts with large pores, low surface area matrices would be better for nickel tolerance. However, these catalysts have less than the optimum matrix activity for cracking bottom and are only approriate when nickel tolerance is the sole objective[4].

III. FUTURE CHALLENGES FOR UTILIZATION OF ZEOLITES CATALYST IN REFINERY

A. *Improvement of Natural Zeolite*

The disadvantage of natural zeolite is the presence of mineral impurities, often in nonuniform compositions and quality, and variable cationic compositions. Natural zeolite occours obviously in Ca, Na, K and Mg forms, and part of these elements can be present also in some of the non zeolite minerals.

Activation of natural zeolite is based on the extraction of alkali and alkaline earth metals form the cationic of the zeolite of single or repeated treatment with aqueous solutions of ammonium salts or mineral acids[2].

Indonesian natural mordenite was activated by a method consisting of a combination of chemical and thermal treatment. Chemical modification was based on the action of sodium hydroxide, ammonium nitrate and hydrochloric acid. Thermal treatment was carried out after a partial chemical modification. After modification, an increased specific surface area, acidity, molar ratio of silica to alumina and catalytic activity of N-hexane cracking was found (Table 2)[7]. Hydrocracking of heavy distillate into lighter distillate was observed to be dependention the acidity of hydrocracking catalysts (Table 3)[6]. The experiment was carried out at Catalyst Laboratory, "LEMIGAS", R/D Centre for Oil and Gas Technology. The operating conditions of the catatest unit is given at Table 4.

For acidic function of cracking and hydrocracking catalysts, the treated natural zeolite must have sufficiently large pores to accomodate most feed molecules; have good stability to high temperature encountered in reaction and regeneration; and have good stability to steam which is formed in regeneration [1].

Natural mordenite is one of natural zeolite which is often a subject of research from the point of view of modifying its properties for cracking catalyts.

B. *Future Challenges for Utilization of Zeolite Catalyst*

Worldwide crude supply are experiencing a modest trend toward heavier and high sulfur content. The Middle East, being traditionally the world's major oil exporting region, will continue to be the principal supplier of lower quality crude in future.

For the periode of 1992-2005, the average annual demand growth rate for light products (gasoline, kerosene and diesel oil) is expected to be higher than that for residual fuel oil. There are three upgrading routes available for bottoms material: i.e. carbon rejection (catalytic cracking), hydrogen addition (hydrocracking) and gasification.

The passage of the clean Air Act Amendment of 1990 in the USA has forced American refineries to install new facilities to comply with stricter specifications for fuels such as gasoline and diesel oil.

Catalytic cracking process has since long been used for reducing the bottom of the barrel and producing high octane gasoline and middle distillate compounds. In recent times, refiners have started cracking process as an olefin generator to facilitate production of alkylates, oligomers and oxygenates (Figure 5). However, catalytic cracking units are quite flexible with respect to feed quality and product pattern. Recent development of the catalytic cracking unit is as an important producer of light olefins for high octane gasoline and petrochemicals.

Today there are more than three hundred catalytic cracking units operated in the world. Cracking catalyst is the highest consumer of catalyst in the refining industry, with a consumption of about 1,000 tonnes per day. The use of zeolites in hydrocarbon cracking now accounts for over 90 per cent of the total consumption of zeolite catalysts [1].

Current federal diesel specifications in the US include a maximum sulfur content 0.05 wt. % and a minimum cetane index of 40. California diesel specs have added restriction of maximum 10 wt. % of aromatics (20 vol. % with cetane improver, if a qualification test is passed). Process technologies currently being selected to meet those specifications included (Figure 6).

Hydrocracking of heavy distillates using dual-function catalyst Ni-Mo supported on a zeolite can effect conversion into high quality middle distillates. The balance between hydrogenation function and acid function of these catalysts may be substantially varied such that a variety of feedstock can be processed, to produce a considerable variety of products.

Based on the increasing role of the cracking processes (catalytic cracking and hydrocracking) for conversion of low quality heavy petroleum fractions into cleaner fuels (gasoline, kerosene, diesel oil), the challenge for future utilization of zeolite in refinery is quite promising.

VI. CONCLUSIONS

Current use of zeolite in refineries is as an acid cracking function of catalytic cracking and hydrocracking processes to convert heavy feeds into light fuels (gasoline, kerosene and diesel oil).

Nowadays, refiners are facing a continuing need to add bottoms processing capacity as a result of gradually deteriorating crude oil quality and flat-to-declining demand for residual fuel oil. Future challenges for utilization of zeolite as an acid cracking function of the cracking process for conversion of low quality heavy petroleum fractions into light clean fuels is promising.

A cooperation in research on the improvement of performance of natural zeolite for zeolite catalyst of cracking process in refinery should be encouraged between Australia and Indonesia.

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