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Catalytic Pyrolysis of Waste Bicycle Tires and Engine Oil to Produce Limonene

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Abstract: NaOH, dolomite and $NiCl_2$ were used as catalysts to examine their effects on co–pyrolysis with waste bicycle tires (WT) and waste engine oil (WEO). The pyrolysis behaviors with catalysts were investigated by thermogravimetric analysis. The activation energy of the catalytic main reaction stage was derived by the Kissinger–Akahira–Sunose (KAS) method under four different heating rates conditions. The calculations show that all three catalysts can reduce the activation energy of the reaction. Co–pyrolysis of WT and WEO with different catalysts was performed in a self–made lab bench at 600 °C to explore the impact on the distribution of three–phase products. The properties of gas and oil products were characterized by FTIR and Py–GC/MS (Agilent 7890B, Santa Clara, CA, USA). With the mixing of catalysts, activation energy (E_α) decreased by 15–30% in the main reaction process. NaOH and dolomite increased the yield of gas by 7% and 10%. NaOH can significantly improve the yield of CH_4. The proportion of limonene in pyrolysis oil increased to 19.65% with 10% NaOH. This article provides a new method for efficiently producing limonene by mixing WT and WEO with NaOH.

Keywords: waste tires; waste engine oil; CH_4; limonene; co–pyrolysis

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1. Introduction

With the continuous development of the transport industry and the rising living standards of humans, the retention of waste tires (WT) has increased dramatically. WT is a common type of hazardous waste. It contains a large amount of volatile organic compounds which are very damaging to the environment and has a high calorific value (33–35 MJ/kg) [1]. The high calorific value of tires is related to its carbon content. Typically, tires have a carbon content of 75–80%. It is difficult to degrade under natural conditions. The WT need to be disposed properly, otherwise they can cause waste of resources and easily form new "black pollution", and cause "secondary damage" to the environment [2]. The WT piled up in the open air create an ideal breeding ground for pests and can also easily cause fires. In recent years, the application of pyrolysis technology to solid waste to recover energy and chemicals has become a good solution to reduce environmental pollution [3]. It can turn waste into value–added alternative energy sources. Pyrolysis gas is a reliable energy sources for the pyrolysis reaction [4]. The oil produced by pyrolysis is fractionated to give a variety of fuel oils [5]. It can also obtain chemical raw materials such as limonene and benzene compounds recovered through secondary reaction [6]. Limonene is a kind of cycloterpene. It is mainly derived from the natural rubber (NR) contained in tires. It can be used as a formula for industrial products (solvents, resins, adhesives). Limonene has broad application prospects and high economic value. It is widely used in the production of foods, spices chemicals, and pharmaceuticals. It can be used as antioxidant, preservative, and perfume additive, and also to synthesize chemical perfume. It has also shown advantages in the fight against cancer. The estimated output of this compound is 50–75 million kilograms per year [7]. According to different purity levels, the market

price of limonene is about 1500–2500 dollars/ton [8]. The traditional method of obtaining limonene is to extract it from citrus or orange peel. Its extraction process is complex and inefficient.

Recently, the content of limonene in WT pyrolysis oil has attracted widespread attention. This provides a new technological route for the efficient production of limonene. A fixed bed reactor was studied to obtain the maximum yield of limonene at a pyrolysis temperature of 475 °C and a heating rate of 20 °C/min, with a value of 7.62 wt.% [9]. Photothermal cracking helps to increase the yield of limonene. The yield can reach up to 8.98 wt.% at 600 °C, and the relative peak areas of gas chromatography–mass spectrometry (GC–MS) results are about 30% [10]. WT started to degrade at about 120 °C less than polyolefins due to the presence of double bonds in the chains of rubbers resulting in weaker bonds in the β position. Due to the obstacles caused by the huge phenyl of SBR, rubber is a poor conductor of heat transfer [11]. During its heating process, it is easy to generate large temperature gradients and local high temperatures, resulting in coking. Previous studies have demonstrated the effect of co–pyrolysis of WT and WEO. The efficiency of heat transfer have been significantly improved. The main pyrolysis temperature has decreased by 50 °C. The generation rate of pyrolysis oil increased. When 20% WEO was added, the yields of H_2 and limonene reached their maximum, increasing by 5.6% and 1.85%, respectively [12]. However, the composition of pyrolysis products is very complex. How to optimize the distribution of products to enhance their utilization value deserves more attention [13]. Many studies have explored the effect of catalysts on the products of WT pyrolysis as Table 1. The effect of NaOH on the properties of waste tires was studied under vacuum conditions. The addition of NaOH greatly improved the yield of pyrolysis oil. Adding 3 wt.% NaOH powder results in a maximum content of 12.39 wt.% limonene in pyrolysis oil [14]. Alkaline catalysts have good catalytic properties and can promote decarbonization and deoxygenation reactions, thereby improving the quality of pyrolysis oil [15]. S Miskah used 25% NaOH and 75% zeolite as catalysts to pyrolysis tires at 400 °C for 3 h. The product obtained an octane number of 113 and a maximum calorific value of 10.2 kcal/g [16]. Nickel–dolomite catalyst can increase the hydrogen production of waste tires. Dolomite is an important low–cost catalyst for tar destruction. $NiTiO_3$ was used to catalyze the production of oil rich in high–value hydrocarbons in WT, resulting in a 50% increase in the yield of oxidized ilmenite [17]. Based on this, this article proposes using catalysts (NaOH, $NiCl_2$ and dolomite) to improve the co–pyrolysis efficiency of WT and WEO in order to optimize the yield of limonene and some high value–added products.

Table 1. The product distribution with different catalyst in previous study.

Catalyst	Yield (wt.%)			Temperature (°C)	Data Source
	Gas	Oil	Char		
CaC_2	34.50	33.50	32.00	400	[18]
MgO	19.30	27.00	53.50	400	[19]
$CaCO_3$	31.90	29.20	38.90	400	[19]
Al_2O_3	21.00	23.20	55.80	400	[20]
$MgCl_2$	16.20	38.20	45.60	407	[21]
HZSM–5	31.00	33.00	36.00	450	[22]
Na_2CO_3	14.60	47.80	37.60	500	[14]
NaOH	13.30	48.10	38.60	500	[14]
Ni + Dolomite	40.00	30.40	29.60	500	[23]

The purpose of this study is to investigate the effects of different catalysts on the co–pyrolysis of WT with 20%WEO, and to explore the enrichment of limonene and other high calorific value gases. In order to explore the influence of catalysts on co–pyrolysis process, thermogravimetric analyzer were employed to investigate the thermal behaviors. The activation energy (E_α) was calculated using the Kissinger–Akahira–Sunose (KAS) method based on the data obtained from thermogravimetric analysis to determine the effect

of the catalyst on the change in activation energy. Pyrolysis experiments were conducted on a small pyrolysis reactor to analyze the changes in the distribution of three–phase products. The effect of catalysts on the yield of pyrolysis gas were explored by using FTIR. Quantitative and semi qualitative analysis of catalytic pyrolysis products was conducted using Py–GC/MS, and the peak area normalization method was used to compare and analyze the concentration and content of limonene. This study proposes a new approach to extract limonene and CH_4 from WT and WEO, providing reference for the industrial application of this technology.

2. Materials and Methods

2.1. Materials

The WT samples in this article were collected from a reprocessing factory of City Qingdao, Shandong Province, China. The main components of tires are NR and synthetic rubber (SR) (50–60%), carbon black (15–25%), and steel (15%). Tires are divided into three types based on their purpose: light vehicle tires (bicycle tires and motorcycle tires), medium vehicle tires (car tires), and heavy vehicle tires (tires for trucks, buses, and large machinery) [24]. Their difference is mainly reflected in the different content of NR and SR. The NR content of light vehicle tires can reach up to 50%. Medium vehicle tires have the lowest NR content. The NR content of heavy vehicle tires is about 30%. The limonene in WT pyrolysis oil mainly comes from NR cracking. In order to obtain more limonene, this article uses bicycle tires as raw materials. First, WT are crushed to powder. The tire powder is placed in a 105 °C drying oven for 24 h. Then the WT powder was screened through a 60–80 mesh screen and sealed in the drying dish for storage. The average particle diameter is 0.2 mm. WEO samples come from a repair factory. The WEO samples were filtered to remove impurities and dried in a drying oven at 70 °C for 24 h. The mixture samples were prepared according to the weight of WEO accounting for 20% of the total weight of the mixture. The amount of catalyst added is 10% by weight of the mixture sample.

2.2. Apparatus and Procedure

2.2.1. TG–FTIR Measurement

The TG–FTIR measurement was carried out using a thermogravimetric (TG) analyzer from Netzsch, Bayern, Germany (Netzsch 209F3) connected with a Fourier transform infrared spectrometer from Thermo Fisher (Nicolet iS20), Waltham, MA, USA. The TG technique provides a powerful analytical tool, combining the quantitative analysis capability of TG with the qualitative analysis capability of FTIR. The sample is subjected to programmed pyrolysis in the TG analyzer and its gaseous products are fed directly into the FTIR spectrometer via a connected tube in order to obtain FTIR spectra [25]. To avoid gas condensation, the connected tube was continuously heated to maintain the temperature. The parameter settings for the experiment are shown in Table 2. Each experiment was repeated three times to exclude errors.

Table 2. Operating conditions of TG–FTIR.

Item		Condition
TG	carrier gas	N_2
	temperature range/°C	20–800
	heating rate/(°C·min^{-1})	15
	sample mass/mg	10
FTIR	frequency ranger/cm	4000–400
	resolution/cm^{-1}	4.0
	scan rate/(scans·s^{-1})	8

2.2.2. Pyrolysis Furnace

Pyrolysis experiments were carried out in a self–made pyrolysis furnace and the three–phase products were collected. The schematic diagram and the physical presentation of the pyrolysis furnace is shown in Figure 1. Before the experiment starts, N_2 is passed through to expel the gas from the tube. The furnace is then programmed to heat up to 600 °C and this temperature was held. The container filled with material is quickly pushed into the furnace to allow it to pyrolysis. The reaction is finished when no more gas is produced. The sample is 10 g mixture and 1 g catalyst.

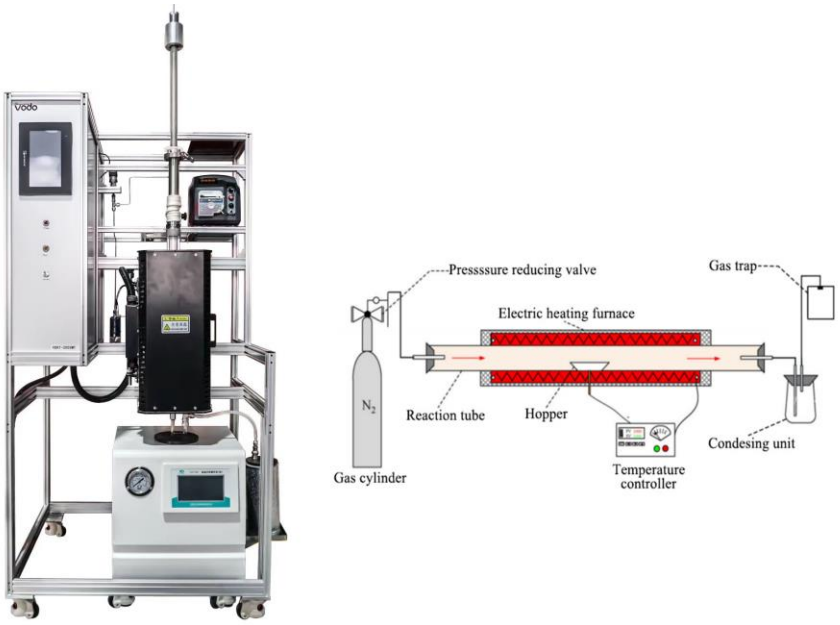


Figure 1. Pyrolysis furnace.

2.2.3. Py–GC/MS Measurement

A pyrolyzer (Frontier EGA/PY3030D, Koriyama, Japan) combined with a gas chromatograph and mass spectrometer (GC/MS, Agilent 7890B, Santa Clara, CA, USA) was used for rapid pyrolysis and product analysis experiments. The experiment parameters are shown in Table 3. The semi–quantitative analysis of each component in pyrolysis oil was carried out using the peak area normalization method. For example, the limonene content is the ratio of the area of the limonene peak as determined by chromatography–mass spectrometry to the total peak area of the pyrolysis oil.

Table 3. Operating conditions of Py–GC/MS.

Item		Condition
Pyrolyzer	furnace temperature/°C	300, 390, 450
	sample amount/mg	10
Gas chromatograph	column style/μm	60 × 0.25 × 0.25
	column temperature	held 40 °C for 3 min, then programmed to 290 °C at a heating rate of 6 °C·min^{-1}
	inlet temperature of column/°C	290
	inlet pressure of column/kPa	50
	split ratio	1:50
Mass spectrometer	interface temperature/°C	290
	scanning range/(m·z^{-1})	15–550
	scan rate/(scans·s^{-1})	5

2.3. Kinetic Analysis

Due to the difference of structural and chemical property, different catalysts have different catalytic mechanisms. In this study, the KAS model free method were used to compare the effect of catalysts on E_α. The overall reaction is described by Equation (1) as follows:

$$A(solid) \rightarrow B(char) + C(volatile) \quad (1)$$

According to Arrhenius theory, the reaction rate equation of solid materials can be expressed as Equation (2):

$$\frac{d\alpha}{dt} = K(T)f(\alpha) = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (2)$$

where α is the rate of conversion, t is the reaction time (s), $k(T)$ is the rate constant of reaction depending on the temperature, $f(\alpha)$ is the mechanism function, A is the pre–exponential factor (min^{-1}), E_α is activation energy(kJ/mol), R is the ideal gas constant (8.314 J/mol·K), T is the absolute temperature (K).

The conversion rate α can calculated by:

$$\alpha = \frac{(m_0 - m_t)}{(m_0 - m_\infty)} \quad (3)$$

where m_0 is the initial mass of sample, m_t is the mass at a certain time, and m_∞ is the final mass. Substituting the heating rate $\beta = dT/dt$ into Equation (4), the kinetic equation of solid matter under non–isothermal conditions can be obtained:

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right)dT \quad (4)$$

Equation (4) has no exact solution; various approximation models were used to solve the complicated part of this equation.

Substituting the Coats–Redfern approximation of the temperature integral into (4), we get the following:

$$\ln\left[\beta/T^2\right] = \ln[AR/EG(\alpha)] - E/RT \quad (5)$$

Activation energy can be obtained by drawing a graph between $1/T$ and $\ln[\beta/T^2]$ and by obtaining slope from drawn straight line.

3. Results and Discussions

The results of proximate and elemental analyses and the predicted HHV (higher heating value) are shown in Table 4. The percentage content of volatile is higher than 60%, especially the content of WLO reaches 97%. This is favorable for ignition. This reduces the amount of heat required for thermochemical reactions to occur and increases the HHV. The yield of pyrolyzed oil and gas can also be promoted. The percentage content of ash is lower than 5–6%. It can be considered as a cleaner fuel. Based on the sustainability concept of biological waste management, zero waste discharge can be achieved.

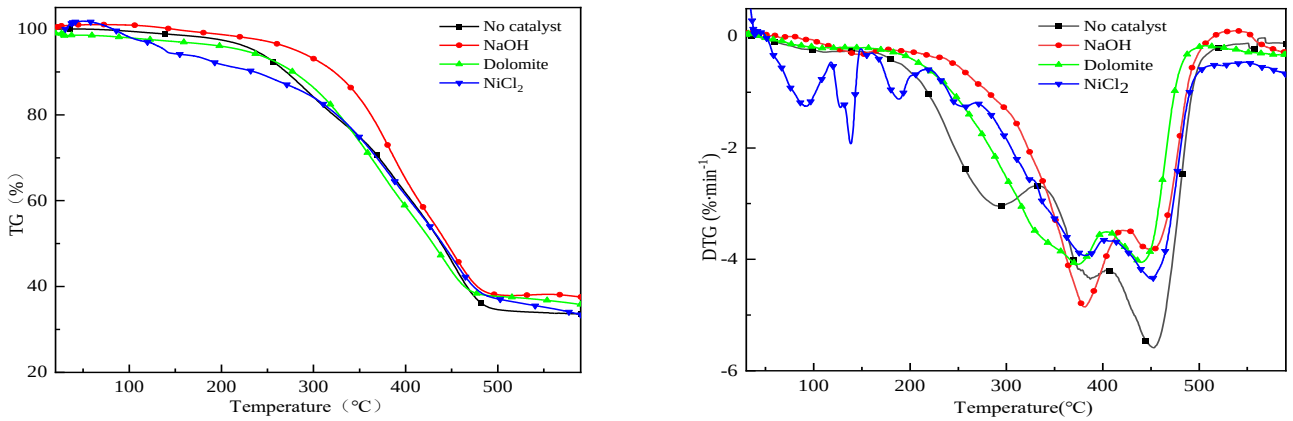
3.1. Thermogravimetric Analysis

Figure 2 shows the TG and DTG curves of sample pyrolysis with different catalyst (No catalyst, NaOH, Dolomite, $NiCl_2$). Catalysts have different effects on pyrolysis, that resulted in different weight loss. It is found in Figure 2 that the weight loss of the case without catalyst is the largest due to the influence of catalyst residue. The influence difference of three catalysts on weight loss is 5%. That means the above catalysts have little significance in promoting the pyrolysis of residual carbon. Pyrolytic char contains more ash. The sample started decomposition at 130 °C and became appreciable at 230 °C. Pyrolysis mainly occurs between 230 and 460 °C. There are two main stages in the pyrolysis process

when no catalyst is mixed. The peak temperatures are 280 °C and 450 °C. The first stage started from 230 °C and ends at 340 °C caused by pyrolysis of NR. The second stage from 340 °C to 500 °C mainly caused by pyrolysis of styrene–butadiene rubber. Information shows the pyrolysis of WEO occurred in the active pyrolysis zone from 250 °C to 450 °C where the dissociation of heavier H/C mainly takes place to produce lower molecular compounds and gases. Catalysts changed the co–pyrolysis process of WT and WEO. The catalysts raised the first peak temperature to 380 °C. NaOH enhanced the weight loss rate of sample. The temperature corresponding to the second weight loss peak is not affected by the catalyst. However, the corresponding weight loss rate decreased. This may be due to the synergistic interaction between small molecular gases produced by co–pyrolysis.

Table 4. Elemental and proximate analysis of feedstock.

	Parameters	Feedstock	
		WT	WEO
Proximate Analysis (wt.%)	Moisture	1.14	0.77
	Volatiles	62.24	97.01
	Fixed Carbon	32.28	1.32
	Ash	4.34	0.90
Elemental Analysis (wt.%)	C	84.35	81.28
	H	6.70	15.61
	O	6.95	2.56
	N	0.39	0.14
	S	1.61	0.41
HHV (MJ/kg)		34.90	41.30



(**a**) TG (**b**) DTG

Figure 2. TG and DTG curves of co–pyrolysis with different catalysts.

3.2. Kinetic Analysis of Catalytic Co–Pyrolysis

Kinetics of blends catalytic co–pyrolysis were determined by using KAS method at the selected degrees of conversion ranging from 0.2 to 0.8. Figure 3 shows the Arrhenius plot of blends with catalysts at different degrees from KAS method. It can be seen from the figure that the catalyst has different effects on the reaction process. Moreover, the variation in activation energy with conversion is revealed in Figure 4. From the comparison of activation energy values, the three catalysts all reduced the E_α required for the reaction process. Among them, the reduction effect of dolomite and $NiCl_2$ is the most obvious. The E_α of sample without catalyst was within the range of 82–89 kJ/mol. The E_α of sample with NaOH was within the range of 65–78 kJ/mol. The difference is that when the conversion is between 0.3 and 0.4, the E_α increased by 10%. This indicates that the reaction resistance is large at this stage. Dolomite and $NiCl_2$ make the E_α reduce to 55–60 kJ/mol and 45–50 kJ/mol, respectively.

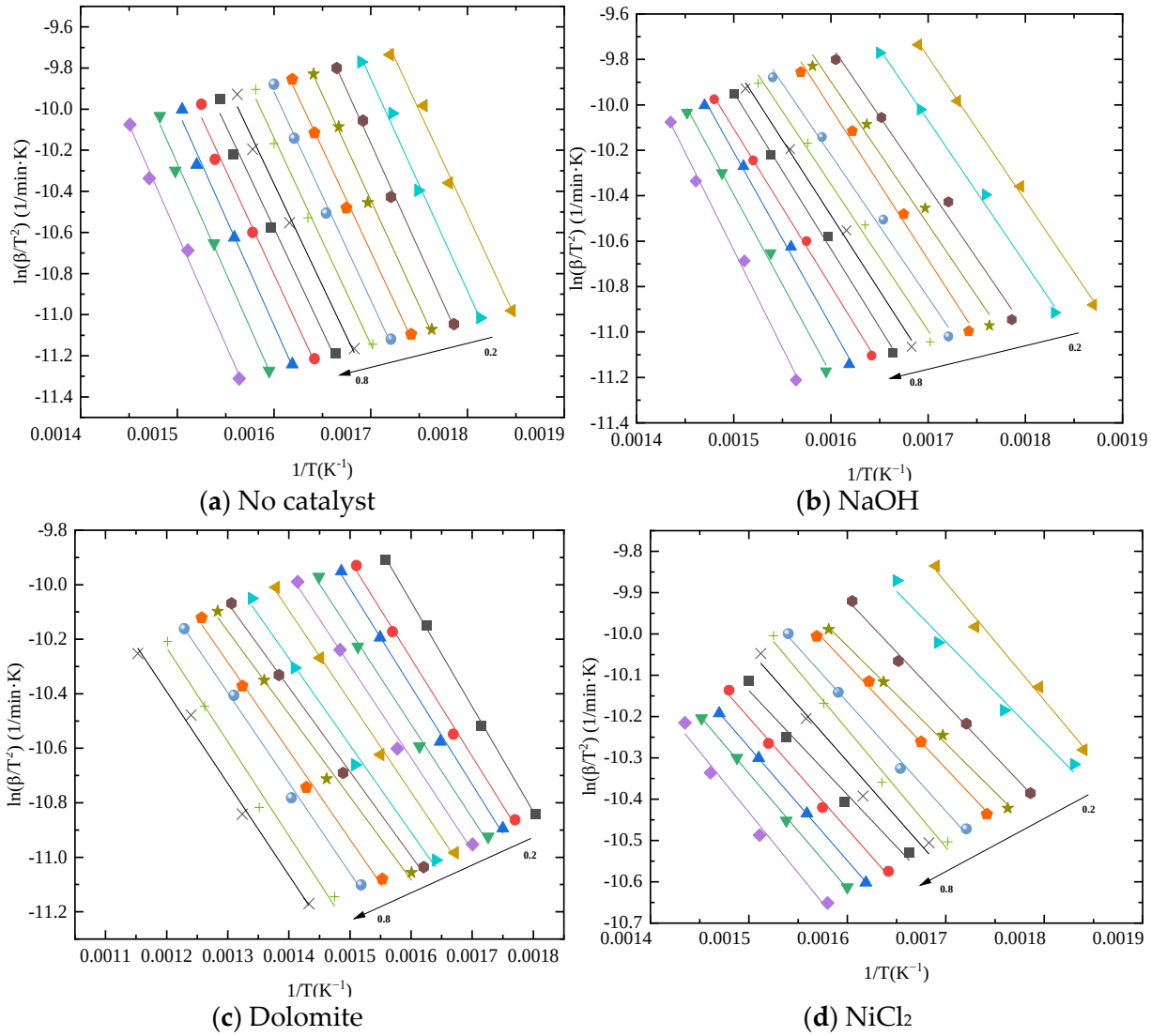


Figure 3. Kinetic plots of blends with different catalysts.

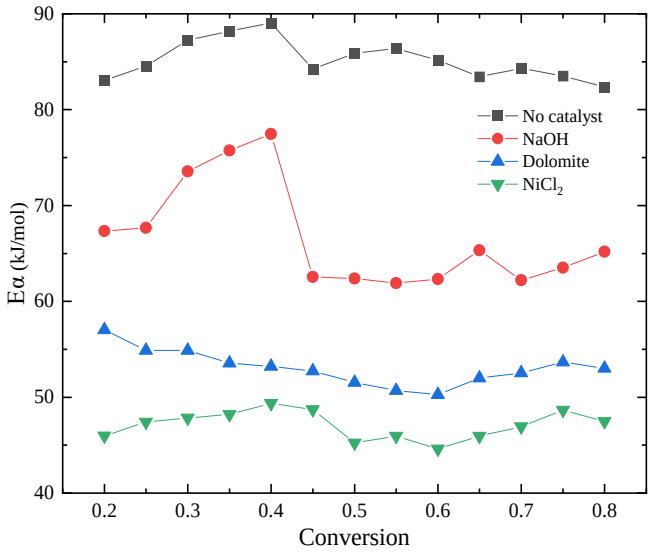


Figure 4. Variation of Eα with conversion.

3.3. Distribution of Co–Pyrolysis Products

As shown in Figure 5, the yield of oil remains at 41 wt% with different catalysts. So, it can be judged that the catalysts has almost no effect on the yield of pyrolysis oil. Mixing dolomite and NaOH increased the yield of gas. The yield of char decreased. This proves that NaOH and dolomite can promote pyrolysis to generate more gases. When there is no catalyst mixing, the yield distribution of pyrolysis products are char 33.6%, oil 40.8%, and gas 25.6%. $NiCl_2$ has little effect on product distribution. The yield of gas increased by 3%, 7%, and 10%, respectively.

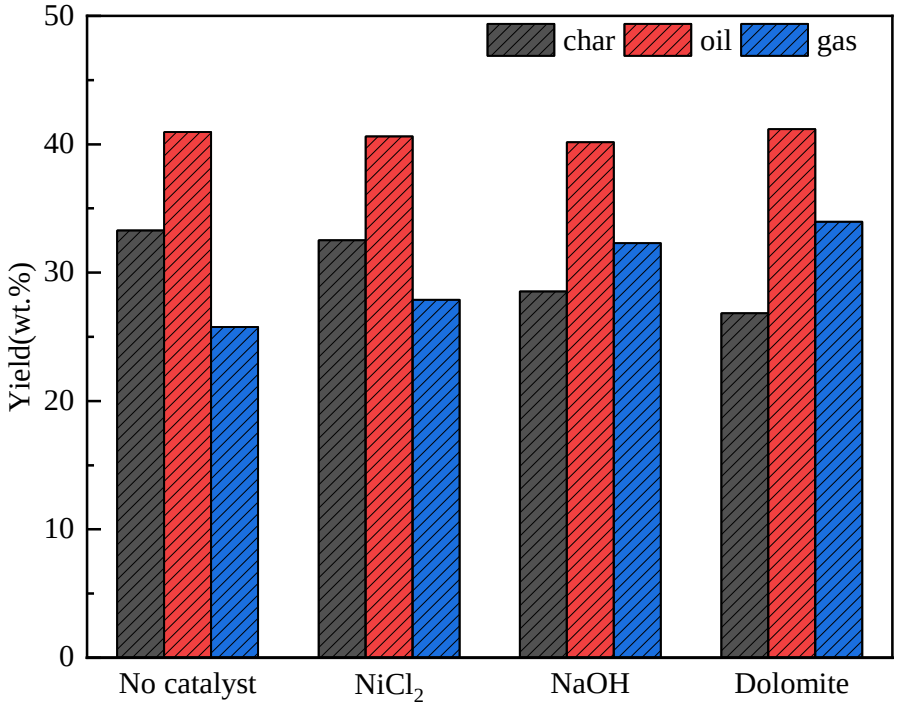


Figure 5. Product distribution of co–pyrolysis with catalyst.

3.4. FTIR Analysis

Based on the DTG curves of Figure 2, the pyrolysis process has three peak temperature values, 300, 390, and 450 °C. The corresponding FTIR spectrogram for the gaseous products at peak temperature values are shown in Figure 6. The IR spectrum of samples with catalysts show absorbance in the range of 1410–1580, 2350–2450, 2750–3000, and 3740–3950 cm. It indicates the main substances are C=O, CO_2, CH_4, and H_2O [25–27]. The largest relative peak area is CH_4. Next is CO_2. At high temperatures, gases containing C=O functional groups such as acids, aldehydes, and ketones precipitate. Comparing with the curve of no catalyst, the absorption peak of CH_4 significant increase with catalyst. NaOH has a great influence on gas release. A small amount of H_2O is also observed.

CH_4 and CO_2 are the main recyclable products in pyrolysis gas. They are the main raw materials for producing synthetic gas through methane drying and reforming method [28]. Figure 7 shows the infrared spectrum of CO_2 and CH_4 from 20–800 °C with different catalysts. Where CH_4 is detected and decomposition starts from 280 °C to 530 °C. CO_2 is released at 260–800 °C. The maximum CO_2 intensity released by NaOH catalytic pyrolysis was at 600 °C. The maximum strength of CH_4 formation is at 400 °C. All the catalysts can enhance the production of CH_4. NaOH shows the most significant effect on the release of CO_2 and CH_4. The NaOH catalyst doubled the relative intensity of CH_4 and CO_2 peaks. From the perspective of manufacturing synthetic gas, NaOH is a better catalyst.

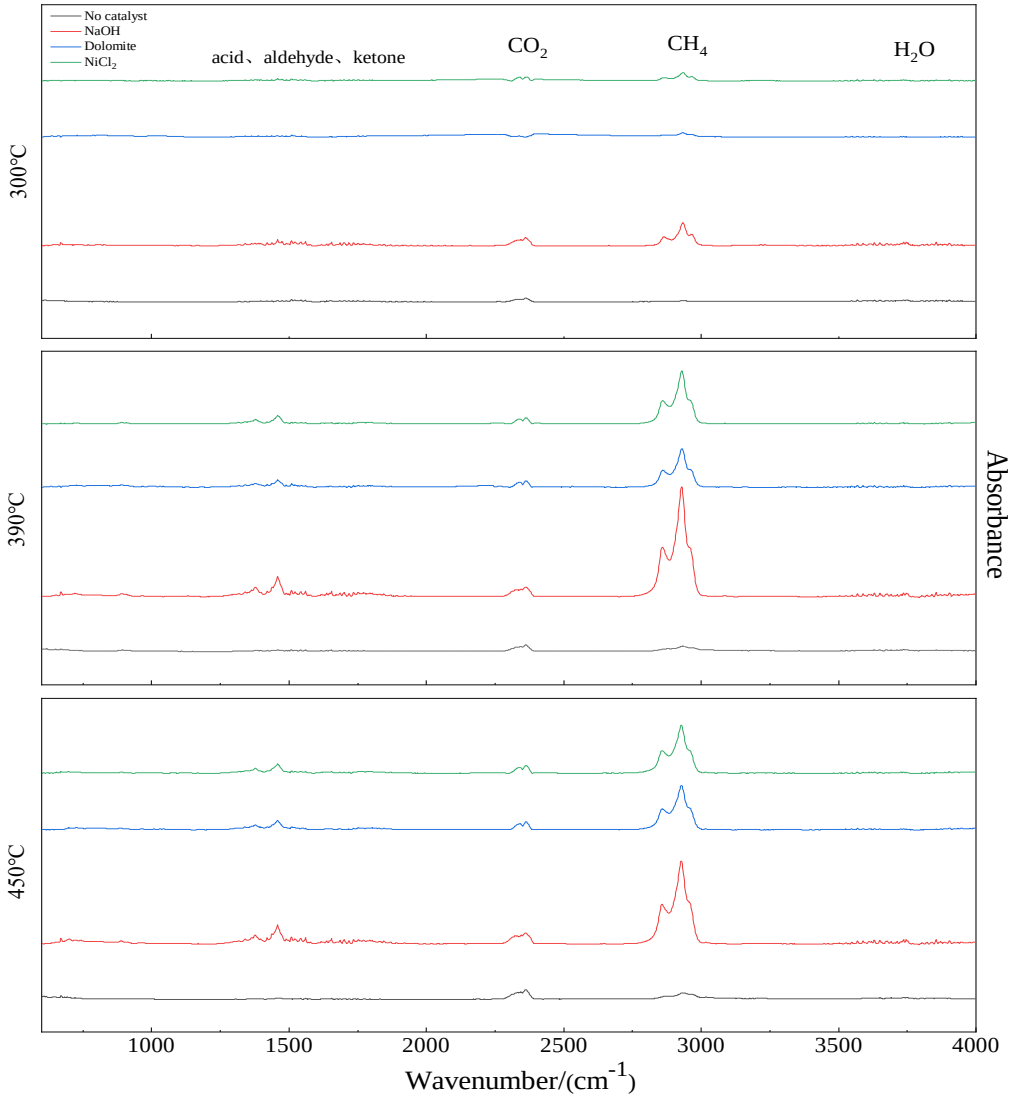


Figure 6. FTIR spectrogram of co–pyrolysis gas at different temperatures.

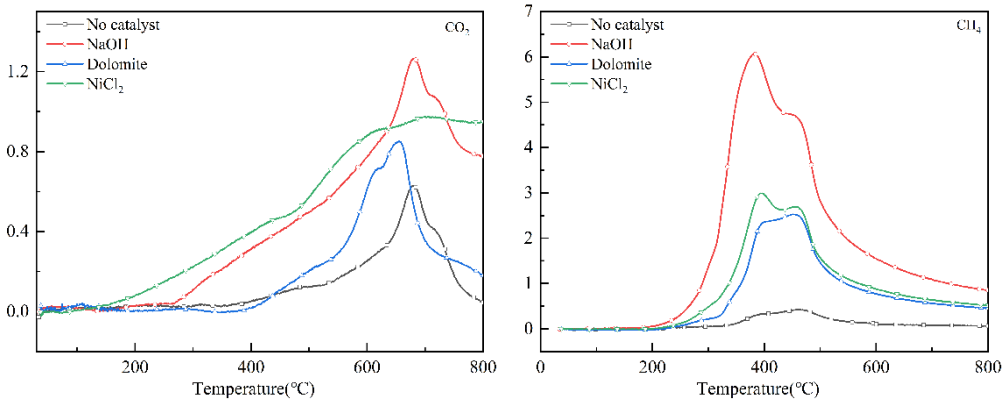


Figure 7. The strength of CO_2 and CH_4 varies with temperature.

3.5. Py–GC/MS Analysis

Figure 8 shows the total ion chromatogram of Py–GC/MS with different kinds of catalysts. It can be seen that the pyrolysis products of blending are mainly composed of macromolecular. The products are mainly acid organics, and macromolecule acids. The

content of olefins, alkanes, and other organic compounds are relatively low. Compared with the co–pyrolysis oil without catalysts, the components detected after using the catalysts was small molecule unsaturated alkenes. This indicates that the three catalysts can effectively promote the decomposition of macromolecular substances into small molecular substances. Compared to the peak plots without catalysts, the peaks of limonene in the plots with catalysts are all enhanced. Table 5 compares the content of limonene in pyrolysis oil and the yield of pyrolysis oil under different operating conditions. By comparison, NaOH has the most significant effect on improving the yield of limonene in pyrolysis oil. The yield reaches 19.65% when with 10% NaOH. Moreover, the yield of oil did not decrease. Compared to previous studies, the yield of limonene has also increased significantly. It provides a reference pathway for the production of limonene.

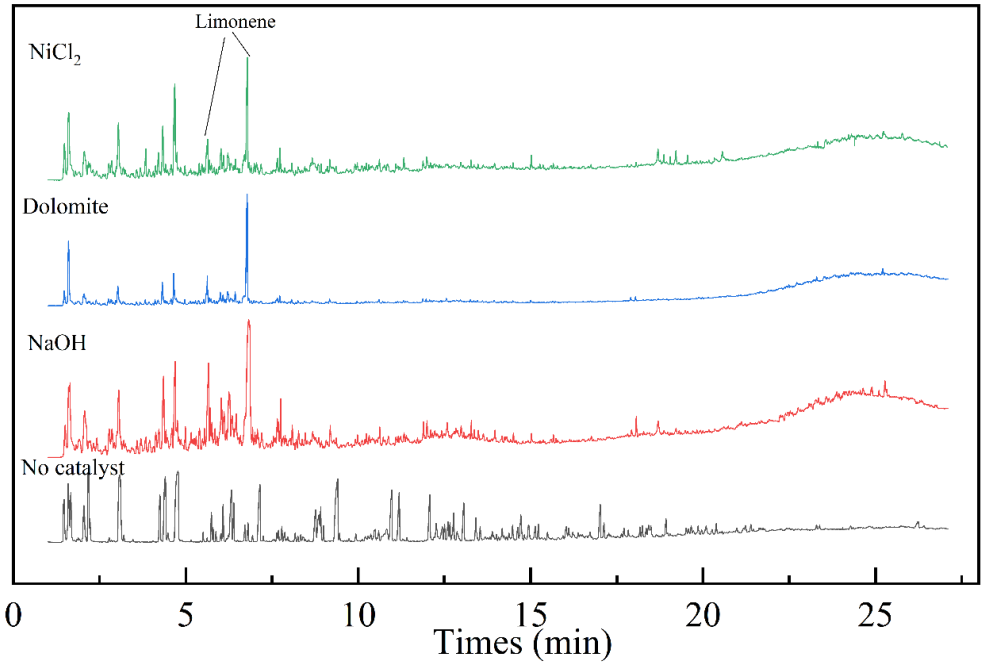


Figure 8. Py–GC/MS chromatograms with different kinds of catalyst.

Table 5. The yield of oil and limonene compared with previous studies.

Material	Catalyst	Method	Oil (%)	Limonene (%)	Data Source
WT + WEO	No	Pyrolysis	41.0	4.99	This work
WT + WEO	10%NaOH	Pyrolysis	41.0	19.65	This work
WT + WEO	Dolomite	Pyrolysis	40.7	16.85	This work
WT + WEO	$NiCl_2$	Pyrolysis	41.5	9.69	This work
WT	No	Pyrolysis	36.6	6.60	[29]
WT	3%NaOH	Vacuum	48.1	11.95	[14]
WT	3%Na_2CO_3	Vacuum	42.0	12.39	[14]
WT	No	Vacuum	32.9	11.97	[14]
WT	No	Pyrolysis	43.0	5.40	[30]
WT	No	Microwave	44.0	9.92	[8]
WT	No	Pyrolysis	49.2	7.90	[31]
WT	No	Pyrolysis	43.4	6.70	[32]

4. Conclusions

In this study, NaOH, dolomite, and $NiCl_2$ are used as the catalysts for co–pyrolysis of WT and WEO to explore improving the yield of limonene. Analysis of three–phase

products obtained from pyrolysis revealed that all three catalysts can improve the yield of pyrolysis gas. Adding catalysts could reduce the value of E_α by 15–30%. NaOH significantly enhances the infrared spectral intensity of CH_4 and CO_2. This is beneficial for the development of synthetic gas. Pyrolysis of WT with 20% WEO and 10% NaOH under conventional conditions can obtain pyrolysis oil containing 19.65% limonene. Compared to other conventional methods, the yield of limonene obtained in this study increased by 70%. The absorption intensity of CH_4 has doubled. This not only enables the utilization of WT and WEO, but also provides an effective way to generate limonene and synthetic gas. However, this article just focused on the differences in results and did not complete the exploration of the essence of the catalytic mechanism. In future research, it is recommended to explore the pyrolysis mechanism of the catalyst.

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