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Ucapan Terima Kasih

Technical Paper

Kinetic Model of Biodiesel Processing Using Ultrasound

Model Kinetika Pengolahan Biodiesel dengan Ultrasound

Bambang Susilo[1]

Abstract

Ultrasound is predicted to be able to accelerate the chemical reaction, to increase the conversion of plant oil into biodiesel, and to decrease the need of catalyst and energy input. The application of ultrasound for processing of biodiesel and the mathematical model were conducted in this research. The result of the experiments showed that the ultrasound increased reaction rate and the conversion of palm oil into biodiesel up to 100%. It was better than the process with mechanical stirrer that the conversion was just 96%. The duration to complete the process using ultrasound was 1 minute. It was 30 to 120 times faster than that with mechanical stirrer. Ultrasound transforms mechanical energy into inner energy of the fluids and causes an increasing of temperature. Simultaneously, natural mixing process undergo because of acoustic circulation. Simulation with experiment data showed that the acceleration of transesterification with ultrasound was affected not only by natural mixing and increasing temperature. The cavitation, surface tension of micro bubble, and hot spot accelerate chemical reaction. In fact, transesterification of palm oil with ultrasound still needs catalyst. It needs only about 20% of catalyst compared to the process with mechanical stirrer.

Introduction

Biodiesel is produced from vegetable oils by converting the triglyceride oil to methyl- or ethylesters with process known as transesterification. The conventional process of transesterification is carried out in a batch system with mechanical stirrer. From this process for a complete reaction needs 30 up to 120 minutes and produces less than 96% conversion of oil to biodiesel (Susilo, 2007).

Ultrasound is the sound which we can not hear due to its high frequency. It is mechanical waves and need a medium for their propagation (Bindal, 1999). The phenomenon of cavitation and accustic mixing occur under aplication of ultrasonic wave in the liquid. Ultrasonic wave is predicted to be able to accelerate the chemical reaction, to increase the conversion of plant oil into biodiesel, and to decrease the need of catalyst and energy input.

The most recent method for biodiesel production is batch transesterification processes. However, generally continuous reactor gives lower production cost and uniform product quality than batch processes. Although the aplication of ultrasounic is hyphothesized improve chemical reaction rate, a few has been reported about the use of ultrasound for improving palm oil trans-esterification. Recently the experimental researches about mathematical model of transesterification of biodiesel processing using ultrasound are not been widely published. The researches are usually carried out in an experimental domain of mechanical stirrer. Although there are a number of kinetics studies in literatur on transesterification of oil with alkohol, only a few of researcher concerned with batch process and no one concerned with kinetic model of ultrasonic aplication for trans-esterification.

The objective of the work was developing dynamic model of transesterification with ultrasound. Two stages of activities were conducted in this research. The first stage was laboratory experiment consist of 2 experiments: (1) effect of ultrasound on palm oil transesterification, (2) effect of ultrasound on disappearance/appearance of tri, di, monoglyceride and esters. The second stage research was model development and validation.

Materials and Methods

Materials

A commercial edible palm oil, a commercial methanol of 95% purity, and a commercial Kalium hydroxide were used in this works. Sulfuric acid 0.6 N was used to neutralize the catalyst and to stop the reaction.

[1] Department of Agricultural Engineering, Faculty of Agricultural Terchnology University of Brawijaya, Malang. Email: susilo@ brawijaya.ac.id

Apparatus

The experimental set up is shown in Figure 1. An Ultrasonic Type Braun-Sonic 2000 instrument consists of ultrasound wave generator, horn and reactor. The generator has frequency and amplitude regulator. It is connected to the horn with cable, that the horn can be moved flexible. The reactor was positioned in a frame. The depth of the horn in reactan is regulated manually. It has two levels frequency. The lower frequency is 19.3 kHz and the upper frequency is 29.53 kHz.
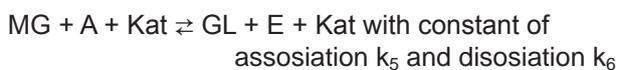
The experiment was worked at maximum frequency and maximum power of ultrasound apparatus. The concentration of catalyst of the first experiment was 10 g KOH/liter of oil (=0.216 M) at reaction times of 30, 60, 120, 240, and 420 seconds. The second experiment was worked at 60 second with concentration of catalyst of 0.216 M, 0.108 M, 0.0648 M dan 0.0432 M.

The process was stopped by neutralization with H_2SO_4 and then centrifuged at 5000 RPM for 5 minutes. The liquid was sepparated carrefully with pipette and rafined twice from catalyst and sulfic acid with aquades (Benitez, 2004). The sample was stored at $0^O C$ to prevent further reaction.

Model Development

The complex reaction of transesterification is caused by glycerol, that has three fatty acid bonds. The model development based on the change of fatty acid chain that be bonded by glycerols. Triglycerides react with methanol produced diglycerides (DG) and methyl ester (E), then diglycerides react with methanol produced monoglycerides (MG) and methyl ester. Furthermore, monoglycerides react with methanol produced methyl ester and glycerols (Nouredinni dan Zu, 1997).

The kinetic model development based on the formation of DG, MG, Kat (Catalyst) and E following the next balanced reaction:

$$TG + A + Kat \rightleftarrows DG + E + Kat \text{ with constant of assosiation } k_1 \text{ and disosiation } k_2$$

$$DG + A + Kat \rightleftarrows MG + E + Kat \text{ with constant of assosiation } k_3 \text{ and disosiation } k_4$$

$$MG + A + Kat \rightleftarrows GL + E + Kat \text{ with constant of assosiation } k_5 \text{ and disosiation } k_6$$

$$TG + A + Kat \rightleftarrows GL + 3E + Kat \text{ with constant of assosiation } k_7 \text{ and disosiation } k_8$$

The catalyst is involved in this model, and always react with reactan compossing methoksid and then compossing product and catalyst. The derivation of mathematical model is like the following formula:

$$\frac{d[TG]}{dt} = -k_1[Kat][TG][A] + k_2[Kat][DG][E]$$

$$\frac{d[DG]}{dt} = +k_1[Kat][TG][A] - k_2[Kat][DG][E] - k_3[Kat][DG][A] + k_4[Kat][MG][E]$$

$$\frac{d[MG]}{dt} = +k_3[Kat][DG][A] - k_4[Kat][MG][E] - k_5[Kat][MG][A][Kat] + k_6[Kat][GL][E]$$

$$\frac{d[GL]}{dt} = +k_5[Kat][MG][A] - k_6[Kat][GL][E] \tag{1}$$

$$\frac{d[E]}{dt} = k_1[Kat][TG][A] - k_2[Kat][DG][E] + k_3[Kat][DG][A] - k_4[Kat][MG][E]$$
$$+ k_5[Kat][MG][A] - k_6[Kat][GL][E]$$

$$\frac{d[A]}{dt} = -\frac{d[E]}{dt}$$

The left hand side of the differential function shows the concentration change of the TG, DG, MG, E, GL and A. It is determined with numerical differential using the Newton's foward difference method (Ayyub dan McCuen, 1996). This equation is valid because the molecul concentration decrease or increase dinamically. The constants of reaction k_1 to k_8 in the right hand side of the equation were
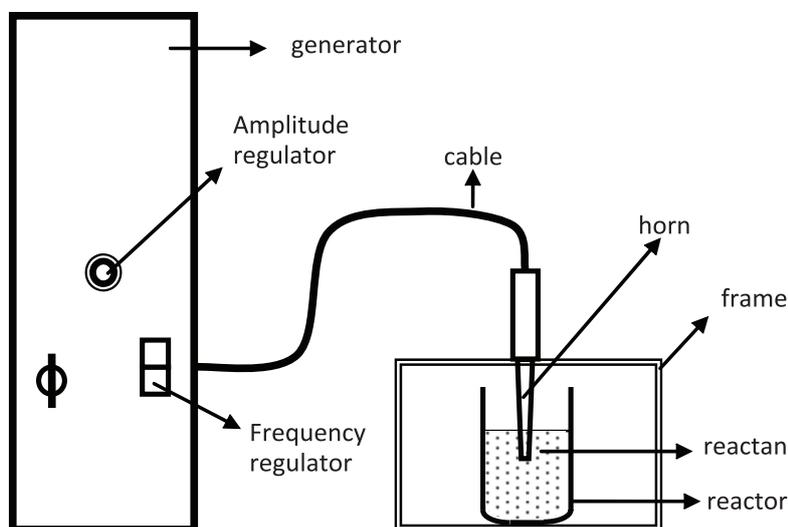

Figure 1. Ultrasonic apparatus

Table 1. Percent differential of ME, TG, DG and MG

Time (minutes)	d(TG)/dt	d(ME)/dt	d(DG)/dt	d(MG)/dt
0.5	-0.30333	64.93167	-40.455	-16.6617
1	-8.93	7.953333	-2.8	2.113333
2	10.355	-14.985	4.825	-0.225
4	-1.62333	2.4	-0.91667	-0.01

found from the matrix multlipication. This matric was formed with first order differential with experimental data of the molecul concentration. Then the matrix is used to develop the following linear equation with 6 unknown variables:

$$
\begin{bmatrix}
a_{11} & a_{12} & a_{13} & a_{14} & a_{15} & a_{16} \\
a_{21} & a_{22} & a_{23} & a_{24} & a_{25} & a_{26} \\
a_{31} & a_{32} & a_{33} & a_{34} & a_{35} & a_{36} \\
a_{41} & a_{42} & a_{43} & a_{44} & a_{45} & a_{46} \\
a_{51} & a_{52} & a_{53} & a_{54} & a_{55} & a_{56} \\
a_{61} & a_{62} & a_{63} & a_{64} & a_{65} & a_{66}
\end{bmatrix}
\begin{bmatrix}
k_1 \\ k_2 \\ k_3 \\ k_4 \\ k_5 \\ k_6
\end{bmatrix}
=
\begin{bmatrix}
b_1 \\ b_2 \\ b_3 \\ b_4 \\ b_5 \\ b_6
\end{bmatrix}
\quad \text{...........(2)}
$$

$$
\varepsilon^2 = \sum_{i=1}^{n} \left[b_1 - \left(a_{i1}k_1 + a_{i2}k_2 + a_{i3}k_3 + \cdots\cdots + a_{i6}k_6 \right) \right] \quad \text{........(3)}
$$

In relation with natural reversible reaction, the constrain of the linear system was using constants of reaction i.e k_1.................. $k_6 \geq 0$. Concentration of TG, DG, MG and E were predicted by the following equation :

$$[TG]_{t_n} = [TG]_{t_{n-1}} + \Delta[TG]_{t_n} = [TG]_{t_{n-1}} + f\left([TG]_{t_{n-1}}, [DG]_{t_{n-1}}, [MG]_{t_{n-1}}, [GL]_{t_{n-1}}\right)$$

$$[DG]_{t_n} = [DG]_{t_{n-1}} + \Delta[DG]_{t_n} = [DG]_{t_{n-1}} + f\left([TG]_{t_{n-1}}, [DG]_{t_{n-1}}, [MG]_{t_{n-1}}, [GL]_{t_{n-1}}\right)$$

$$[MG]_{t_n} = [MG]_{t_{n-1}} + \Delta[MG]_{t_n} = [DG]_{t_{n-1}} + f\left([TG]_{t_{n-1}}, [DG]_{t_{n-1}}, [MG]_{t_{n-1}}, [GL]_{t_{n-1}}\right)$$

$$[E]_{t_n} = [E]_{t_{n-1}} + \Delta[E]_{t_n} = [E]_{t_{n-1}} + f\left([TG]_{t_{n-1}}, [DG]_{t_{n-1}}, [MG]_{t_{n-1}}, [GL]_{t_{n-1}}\right)$$

The simulation model was developped with finite difference method in the range of experimental reaction time. This time range was divided in the part of 1 second (Δt = 1), that the concentration of TG, DG, MG and E can be predicted each 1 second. The output of simulation was tested with experimantal data to evaluate validity of the model.

Results and Discussion

The experimental results for the concentration of the reaction mixture during the reaction in the significant range are shown in Figure 2. The highest concentrations of DG and MG were observed at 30 seconds. Their levels then decreased and
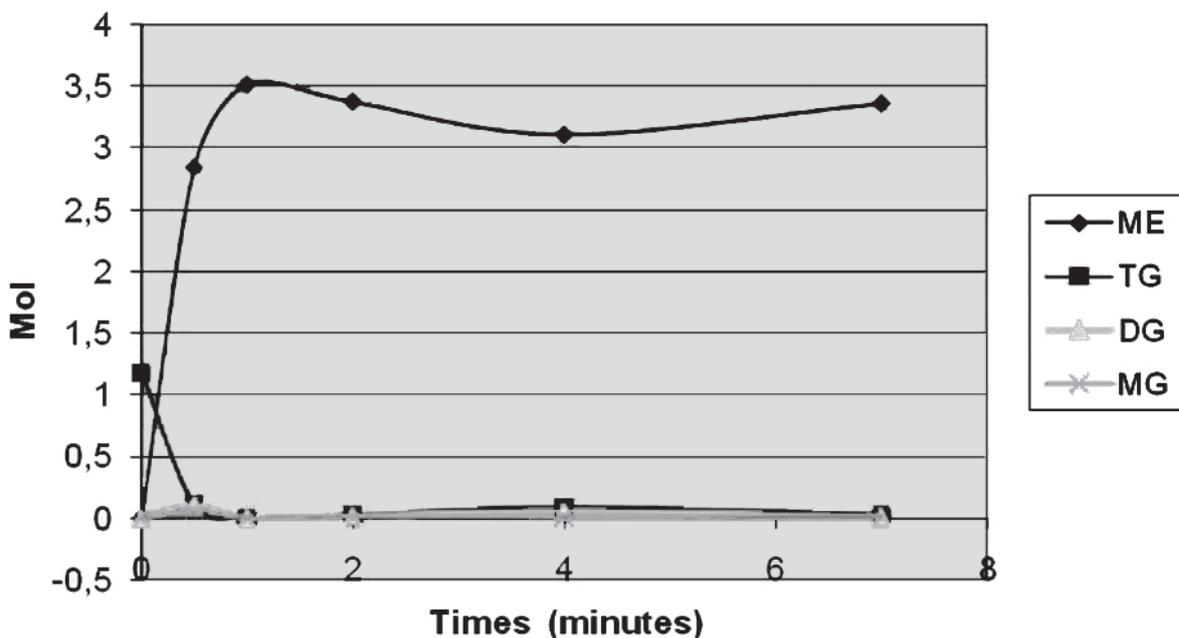

Figure 2. Mol composition of ME, TG, DG and MG

Tabel 2. Molarity differential of ME, TG, DG and MG (mol/second)

Time (minutes)	d(ME)/dt	d(TG)/dt	d(DG)/dt	d(MG)/dt	d(GL)/dt
0.5	2.282308	-0.00357	-0.67764	-0.48365	0.760769
1	0.279555	-0.10512	-0.0469	0.061345	0.093185
2	-0.52671	0.121895	0.080821	-0.00653	-0.17557
4	0.084359	-0.01911	-0.01535	-0.00029	0.02812

disappeared at 60 seconds to reach equilibrium. After 60 seconds TG disappeared, but a little of DG and MG still remained. The peak of ester is reached at 60 seconds, that the conversion of triglycerides to biodiesel was up to 100%.

The differentiation of mole concentrations respect to time on the left hand side of Eq. (1) was calculated from the experimental mole concentrations at various reaction times by three-points numerical differential formulas. The experimental results for the percent differential of TG, DG, MG dan E are shown in Table 1, and the concentration differential of TG, DG, MG dan E are shown in Table 2. Moreover the mathemathical model was constructed at molar ratio of 0.256 M KOH catalyst and molar ratio of methanol to oil 6 : 1.

The value of the matrics element of equation (2) are found by the following formula :

$a_{11} = -[TG][A], a_{12} = [DG][E], a_{13} = a_{14} = a_{15} = a_{16} = 0$

$a_{21} = [TG][A], a_{22} = -[DG][E], a_{23} = -[DG][A], a_{24} = [MG][A], a_{25} = a_{26} = 0$

$a_{31} = a_{32} = 0; a_{33} = [DG][A], a_{34} = -[MG][E], a_{35} = -[MG][A], a_{36} = [GL][E]$

$a_{41} = a_{42} = a_{43} = a_{44} = 0, a_{45} = [MG][A], a_{46} = -[GL][E]$

$a_{51} = [TG][A], a_{52} = -[DG][E], a_{53} = [DG][A], a_{54} = -[MG][E], a_{55} = [MG][A],$
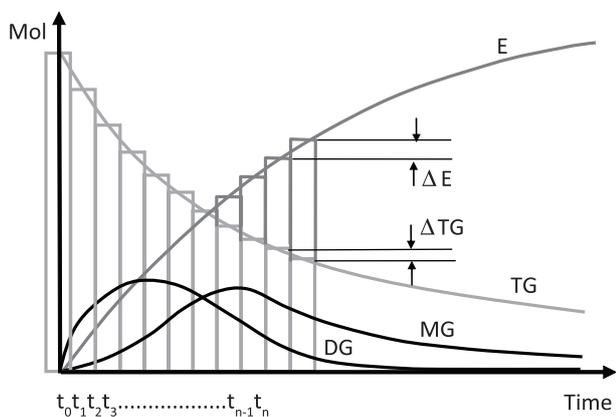
$a_{56} = -[GL][E]$

Figure 3. Schematic model of ester production at times t_n

Table 3. Constants of transesterification rate with ultrasound

No.	Constant	Value (Mol/seconds)
1	k_1	0.000165
2	k_2	0.0001
3	k_3	0.01878
4	k_4	0.2715
5	k_5	0.1602
6	k_6	0.0036

Then all of the first order differentials are devided by the concentration of the catalyst. The result is the right hand sight constants of the matrics.

$$\frac{1}{[Kat]}\frac{d[TG]}{dt} = b_1, \frac{1}{[Kat]}\frac{d[DG]}{dt} = k_1, \frac{1}{[Kat]}\frac{d[MG]}{dt} = b_3,$$

$$\frac{1}{[Kat]}\frac{d[GL]}{dt} = b_4, \text{ dan } \frac{1}{[Kat]}\frac{d[E]}{dt} = b_5$$

The elemen of silmultaneous equation (2) are found completely and then by elimination of the matric, the value of k_i can be shown in Table 3.

Model of Triglycerides Conversion to Methyl Ester

The governing set of the model equations characterizing the stepwise reactions for transesterification of TG, without the shunt reaction, are as following. Methyl ester is producted by the reaction of TG and A, DG and A, and MG and A. Methyl ester at time t_n is the accumulation of E at t_{n-1} and the production of methyl ester between t_{n-1} and t_n. The change of methyl ester concentration is the function of TG, DG, MG and A at t_{n-1}. The concentration of TG, DG, MG and A at t_n are the concentration of TG, DG, MG and A at t_{n-1} substracted by TG, DG, MG and A convertted to methyl ester betwen t_{n-1} and t_n.

Testing of the Model

The experimental and simulation results for the concentration of the reaction mixture during the reaction in the significant range are shown in

Figure 4. Moreover, Figure 4 shows the coeficient of determination was 95%. It shows that the simulation concentrations of all compositions fit well with experimental concentrations. It is also clearly show that the model was good enough to predict the concentrations of ester respect to time.

The production rate of ME with ultrasound as in Figure 4 starts with a sudden surge followed by a lower production rate as reaction approaches equilibrium. It was different to the production of biodiesel with mechanical stirrer. Noureddini and Zhu (1997) wrote that the production with mechanical stirrer shown a sigmoidal pattern (S-shape) for production of ME. This pattern consists of a slow rate at the beginning followed by a sudden surge and finally a slow rate again.

Transesterification with ultrasound did not show the initial mass transfer-controlled region, that there was no S-shape curve and no lag time at the initial stage. The reaction direct to the kinetically controlled region. It was occured because of perfect mixing with ultrasound that affecting good diffusion between alcohol and oil. Noureddini and Zhu (1997)

explain, if a sufficient mixing is supplied, a lag time of a mass transfer-controlled region can be eliminated. It drives the reaction to be homogeneous for all reaction times even in the initial stage of the reaction (Leevijit, *at.al.*). In addition, aplication of ultrasound in liquid creates cavitation and hot spot, that it increases all of chemical reaction (Suslick *et.al.*, 1999).

Figure 2 shows that the optimum reaction times with ultrasound was 60 second, that the conversion of triglycerides was 100%. Based on this result, the experiment with lower catalyst was done with 60 minutes reaction times. The simulation was contructed refer to equation (1) and be tested with experimental data. Figure 5 shows experimental and simulation data. It seems that the value was significantly different, but the trend of the graph was almost closed.

Figure 5 also show that simulation concentrations of catalyst concentrations fit well with experimental concentrations. The coeficient of determination is 0.99. It provides a satisfactory mechanism for transesterification with ultrasound.
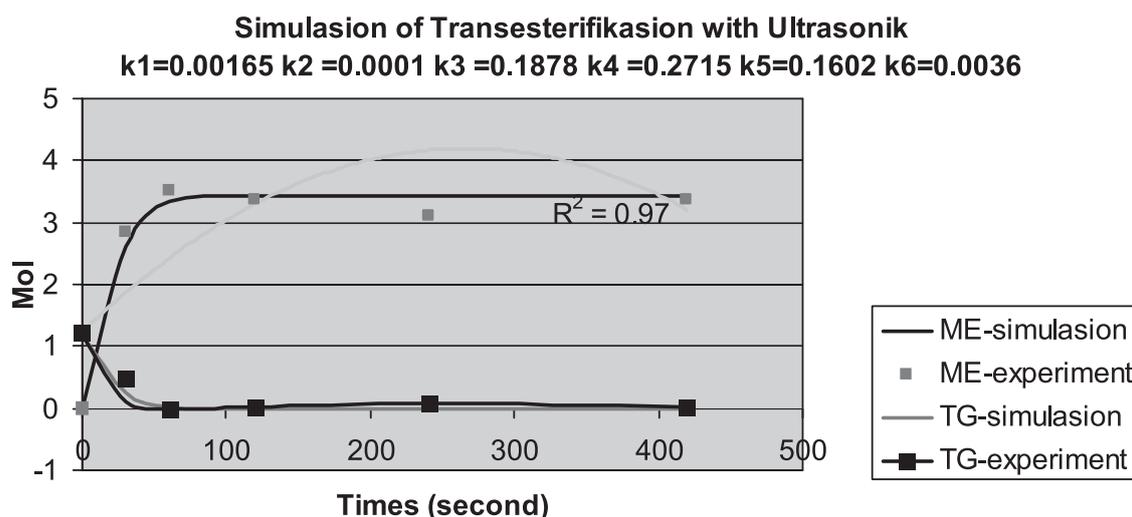

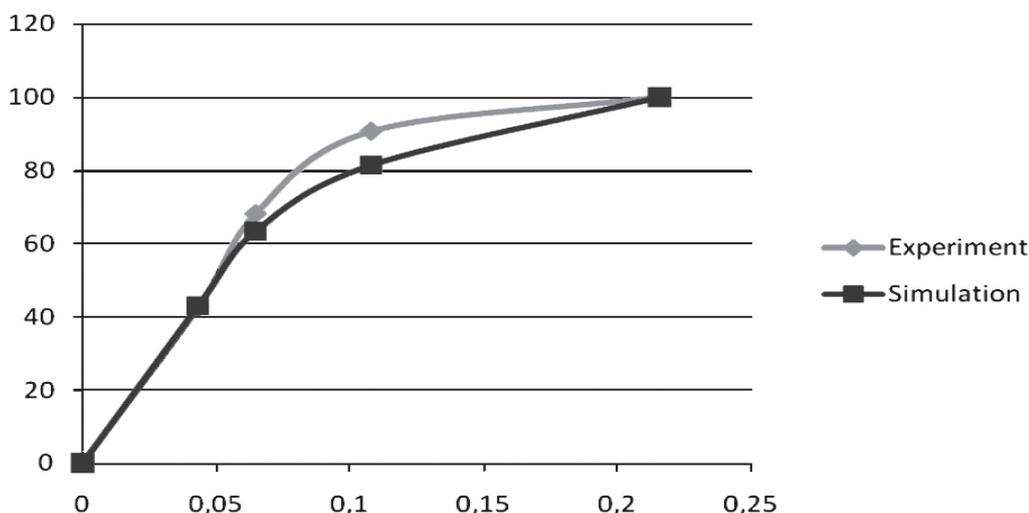Figure 4. Simulation of ME production with ultrasound

Figure 5. Simulation of ME production with ultrasound respect to catalyst concentration

Conclusions

Transesterification with ultrasound converts triglycerides to methyl ester more effectif than that with mechanical stirrer. The conversion was up to 100% with 29.57 kHz ultrasound for reactant volume 125 ml at 60 seconds reaction times. The kinetics model was fit well to predict biodiesel production with ultrasound.

Acknowledgements

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