Biodiesel production from residual edible oils catalyzed by ionic liquid hydrogen sulfate 1-butyl-3-methylimidazolium [BMIM][HSO$_4$]

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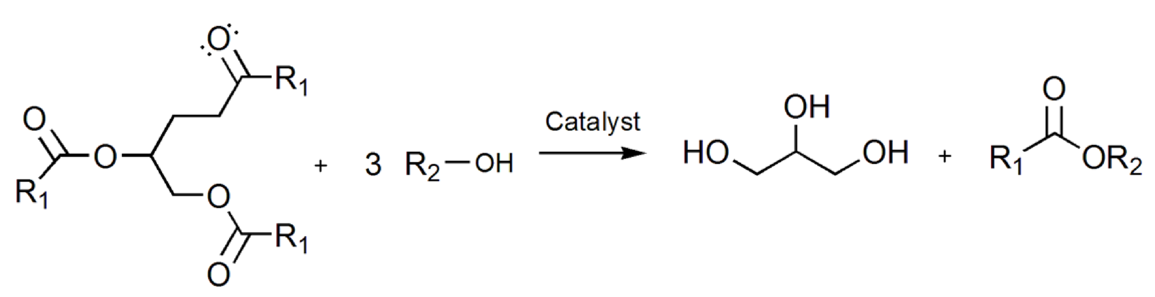
BACKGROUND AND LITERATURE REVIEW

BIODIESEL

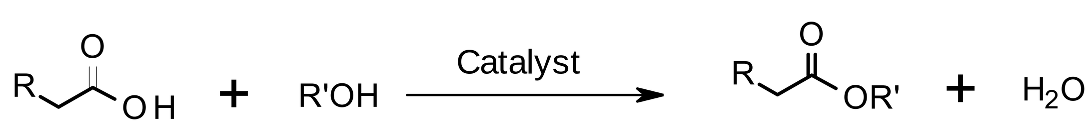
Biodiesel is defined as a mixture of monoalkyl esters of long chains of fatty acids (FAME). which can be obtained by converting vegetable oils or animal fats through transesterification or esterification reactions. Due to its numerous advantages. such as biodegradability. low viscosity. high flash point and low environmental impacts. it has the potential to be used directly in diesel engines. without any modification.[2]

PRODUCTION METHODS

Transesterification is a favorable reaction to obtain fuel from triglycerides.



Esterification is an option for the conversion of free fatty acids (FFA) present in oils.



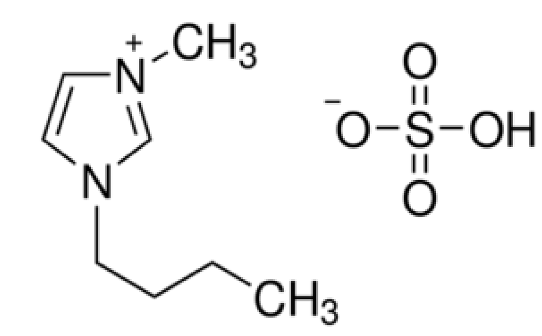
CATALYST

In both reactions. the presence of **catalysts** is required for an effective conversion.

- Alkali catalysts are not capable of catalyzing the esterification reaction and may lead to the saponification reaction.
- Acid catalysts promote both transesterification and esterification reactions but present several drawbacks.

IONIC LIQUIDS (IL)

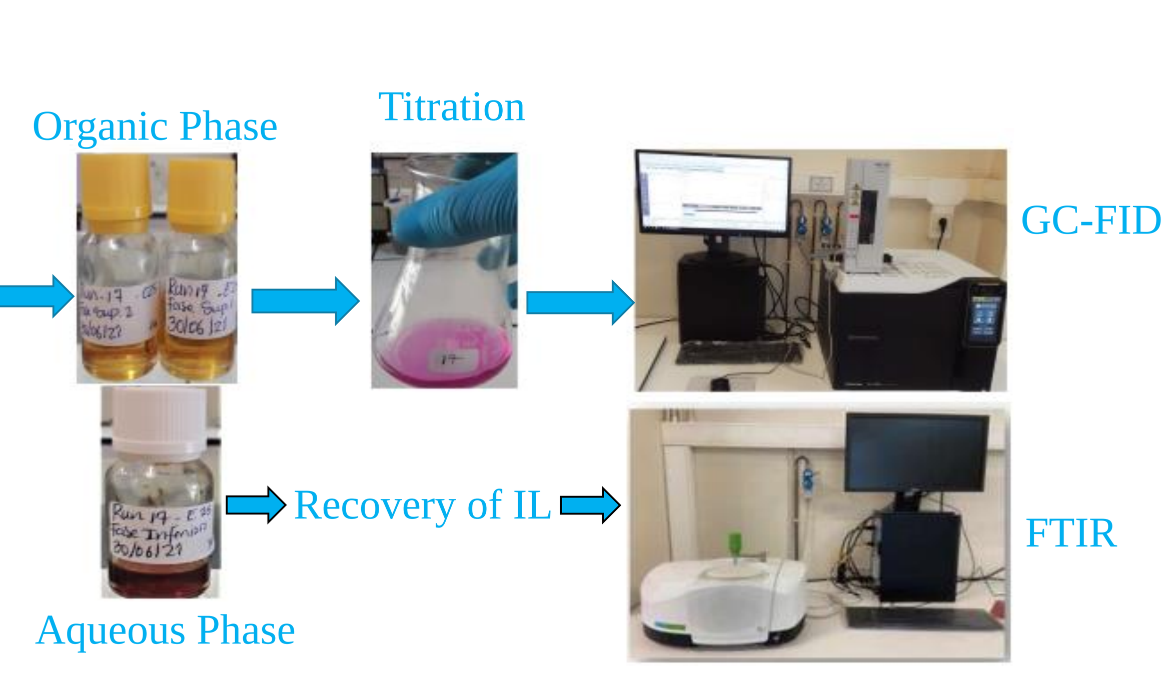
IL are environmentally-friendly catalysts resulting in high conversions in biodiesel production. They have possibility of designing a specific molecule and ability to recycle and reuse.[1]



1-butyl-3-methylimidazolium hydrogen sulfate [BMIM]HSO4

EXPERIMENTAL METHODOLOGY

SYNTHESIS AND CHARACTERIZATION OF BIODIESEL:



RESPONSE SURFACE METHODOLOGY – (BOX-BEHNKEN DESIGN):

- The methodology establishes a set of 27 runs for the quantification of the influence of each factor on the responses.
- Study of 2 responses: Reduction of Acidity and Content of FAME of the biodiesel sample produced.
- Responses measured by gas chromatography and acid-base volumetric analysis.
- A reaction temperature of 65ºC is maintained for all experiments.

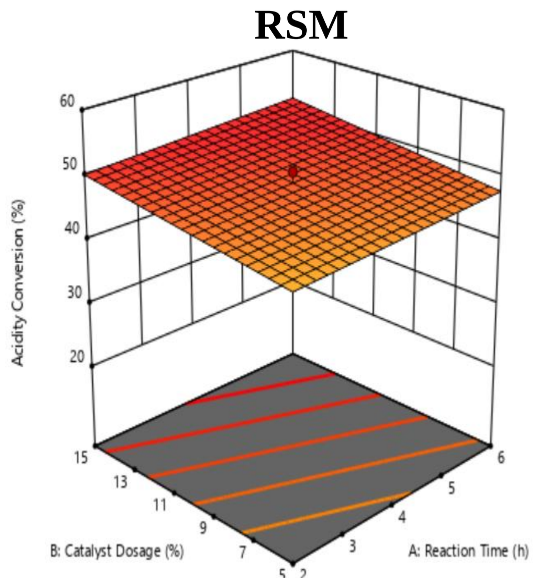
		LEVEL		
FACTOR	NAME	-1	0	1
A	Reaction Time(h)	2	4	6
B	Catalyst Dosage (%)	5	10	15
C	Molar Ratio oil:metanol	5	15	15
D	Incoporation Oleic Acid (%)	20	60	60

- Response Surface Methodology (RSM), from a Box-Behnken experimental design of a 3^4 factorial.

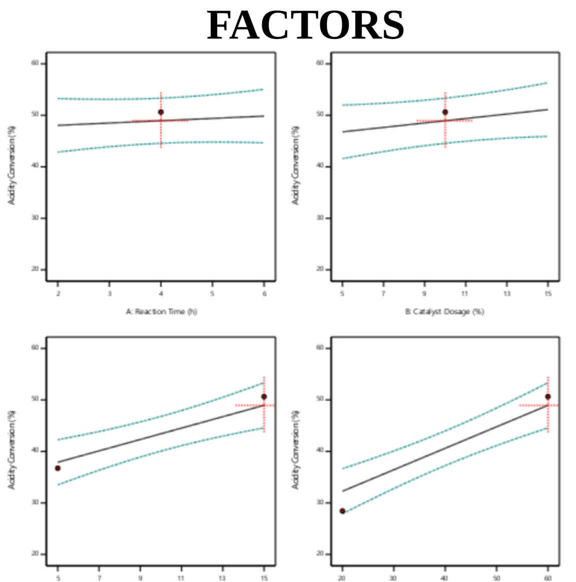
RESULTS and DISCUSSIONS

RESPONSE 1 – ACIDITY CONVERSION:

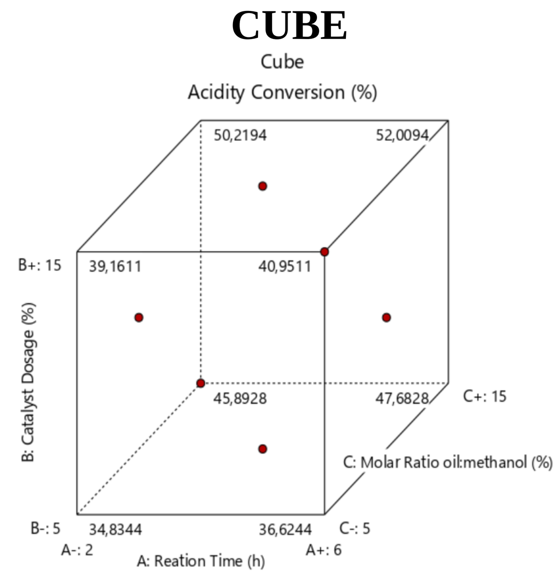
RSM



FACTORS



CUBE



RESPONSE 1: ANOVA ANALYSIS:

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1267,47	4	316,87	14,46	< 0.0001	significant
A-Reaction Time	9,61	1	9,61	0,4386	0,5147	
B-Catalyst Dosage	56,16	1	56,16	2,56	0,1237	
C-Molar Ratio oil:methanol	366,86	1	366,86	16,74	0,0005	
D-Incorpotation of Oleic Acid	834,83	1	834,83	38,09	< 0.0001	
Residual	482,17	22	21,92			
Lack of Fit	468,51	20	23,43	3,43	0,2498	not significant
Pure Error	13,66	2	6,83			
Cor Total	1749,63	26				

Coefficients in Terms of Coded Factors

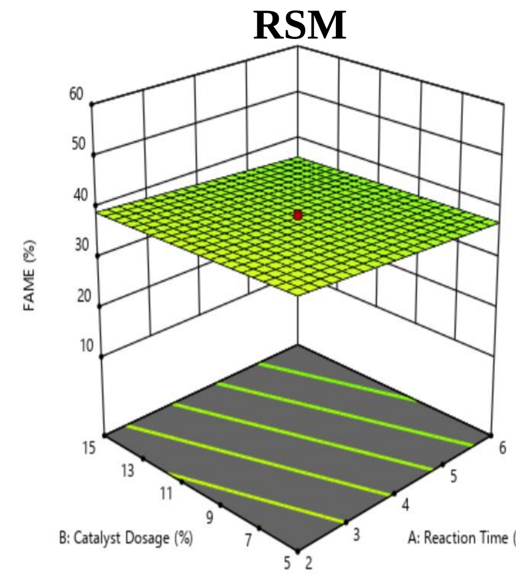
Intercept	A	B	C	D	AB	AC	AD	BC	BD	CD
+35,08	+0,8950	+2,16	+5,53	+8,34	+0,7650	-2,42	-0,1425	+0,8325	+5,71	+1,61

$$Y = 35{,}08 + 0{,}8950A + 2{,}16B + 5{,}53C + 8{,}34D + 0{,}7650AB - 2{,}42AC - 0{,}1425AD + 0{,}8325BC + 5{,}71BD + 1{,}61CD$$

- The Model F-value of 14,46 implies the model is significant. There is only a 0,01% chance that an F-value this large could occur due to noise.
- P-values less than 0,0500 indicate model terms are significant. In this case C, D are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

RESPONSE 2 – FAME CONVERSION:

RSM



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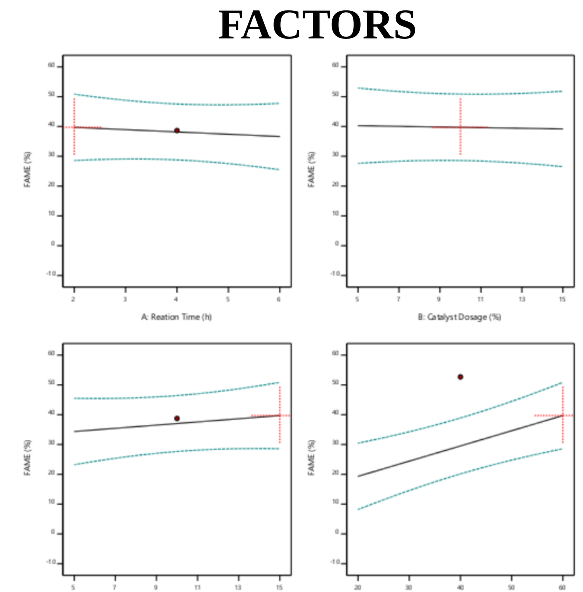
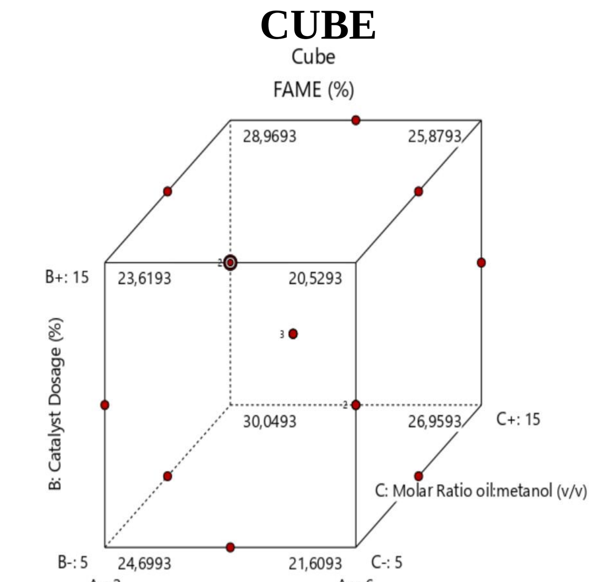


CUBE



REPONSE 2: ANOVA ANALYSIS

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1365,68	4	341,42	3,40	0,0262	significant
A-Reaction Time	28,64	1	28,64	0,2850	0,5988	
B-Catalyst Dosage	3,50	1	3,50	0,0348	0,8537	
C-Molar Ratio oil:metanol	85,87	1	85,87	0,8543	0,3654	
D-Incorpotation of Oleic Acid	1247,66	1	1247,66	12,41	0,0019	
Residual	2211,22	22	100,51			
Lack of Fit	2196,71	20	109,84	15,14	0,0637	not significant
Pure Error	14,51	2	7,25			
Cor. Total	3576,89	26				

Coefficients in Terms of Coded Factors

Intercept	A	B	C	D	AB	AC	AD	BC	BD	CD
+25,29	-1,55	-0,54	+2,68	+10,2	+8,59	-7,08	+1,5	-4,53	-3,06	-0,2525

$$Y = 25{,}29 – 1{,}55A - 0{,}54B + 2{,}68C + 10{,}2D + 8{,}59AB - 7{,}08AC + 1{,}5AD - 4{,}535BC - 3{,}06BD - 0{,}2525CD$$

- The Model F-value of 3,40 implies the model is significant. There is only a 2,62% chance that an F-value this large could occur due to noise.
- P-values less than 0,0500 indicate model terms are significant. In this case D is a significant model term. Values greater than 0.1000 indicate the model terms are not significant.

CONCLUSIONS

- The best result in terms of FAME's was obtained with the following conditions: reaction time of 2 hours, catalyst dosage 10% wt, oil:methanol molar ratio of 1:15 and incorporation of oleic acid in the UCO (Used Cooking Oil) of 40%.
- Only the Esterification reaction has occurred. This conclusion is supported by the following reasons: absence of glycerol formation; FAME contents below the incorporation % of oleic acid; FAME consisting essentially of methyl esters of oleic acid.

REFERENCES:

1. Troter D. Z.; Todorović Z. B.; Đokić-Stojanović D. R.; Stamenković O. S.; Veljković V. B. *Renew. Sust. Energ. Rev.* **2016**, *61*, 473.
2. Yaakob O.; Mohammad M.; Alherbawi M.; Alam Z. *Renew. Sust. Energ. Rev.* **2013**, *18*, 184.

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